

MILD COAL PRETREATMENT TO ENHANCE LIQUEFACTION REACTIVITY

R.L. Miller, K. Shams, and R.M. Baldwin

Chemical Engineering and Petroleum Refining Department
Colorado School of Mines
Golden, Colorado 80401

ABSTRACT

This paper reports results from an on-going process development study in which coal is converted to liquid products at relative mild reaction conditions. The process consists of three main steps: 1) mild pretreatment of the feed coal at ambient conditions using methanol (or other common organic solvent) and a trace amount of hydrochloric acid to enhance dissolution reactivity and dry the coal, 2) low severity thermal dissolution to obtain a very reactive coal-derived residual intermediate product amenable to upgrading, and 3) catalytic upgrading of the residual products to distillate liquids. We have found that mild pretreatment of Wyodak subbituminous coal using methanol/HCl can provide an improvement in THF conversion of greater than 30 wt% at 350°C reaction temperature. Possible explanations for the observed reactivity enhancement include mild alkylation at oxygen sites in the coal's organic phase, leaching of selected elements from the coal's mineral matter phase, or formation of chlorinated species such as FeCl_3 , which are known to be active coal dissolution catalysts.

INTRODUCTION

Much of the recent research in direct coal liquefaction seeks to develop methods for dissolving coal at low reaction severity (defined as temperatures below 350°C and pressures of 1000-1500 psi). The incentives for developing a viable low severity liquefaction process are numerous; they include: 1) reduced hydrocarbon gas production resulting in reduced feed gas consumption and enhanced hydrogen utilization efficiency, 2) suppressed retrogression of primary coal dissolution products resulting in enhanced distillate and residuum product quality, 3) production of high boiling residuum which is less refractory and thus more amenable to catalytic upgrading in a conventional second-stage hydrocracker, 4) substitution of less expensive off-the-shelf vessels, piping, valves, pumps, etc. in place of expensive, custom-designed units, and 5) less severe slurry handling and materials of construction problems as a result of lower operating temperatures and pressures.

Researchers at several locations including the Pittsburgh Energy Technology Center (1), the University of North Dakota Energy and Environmental Research Center (2), Carbon Resources, Inc. (3), and the Colorado School of Mines (4) have investigated various methods for improving coal reactivity and liquid yields at mild reaction conditions. These studies showed that coal can be readily converted to tetrahydrofuran (THF) soluble products via selective chemical attack rather than thermal bond scission, but that the rate and extent of coal dissolution at mild conditions is strongly dependent upon intrinsic coal reactivity. Thus the problem of optimizing low severity liquefaction conversion becomes one of maximizing coal reactivity at these conditions.

The objective of this paper is to present recent experimental data in which mild chemical pretreatment using methanol or other common organic solvent and hydrochloric acid is used as a method to improve intrinsic coal reactivity at low reaction severity. The original basis for this work derives from studies by Sternberg (5), Liotta (6), Sharma (7) and others where alkylation was used as a method for rendering coal soluble in THF or toluene to aid in structural analysis. Sharma's work demonstrated the ability to mildly alkylate coal using alkyl alcohols. Limited work has been reported in which the liquefaction reactivity of alkylated coals has been studied. Schlossberg et al. (8) measured the reactivity of alkylated Wyodak subbituminous and Illinois #6 bituminous coals in tetralin at 427°C, 1500 psi hydrogen pressure and 130 min. reaction time. A 10-21 wt% (maf and alkyl group-free basis) increase in cyclohexane conversion was noted for the alkylated coals.

EXPERIMENTAL PROCEDURE

The entire suite of eight coals from the Argonne Premium Coal Sample Bank was used as the source of feed coals for this study. Ultimate analyses for these coals are listed in Table I. Coal samples were stored under argon in sealed ampules prior to pretreatment and liquefaction experiments.

Pretreatment experiments were performed using a liquid phase technique we developed based on the gas phase alkylation chemistry reported by Sharma (2). Coal was pretreated by suspending 5 g of undried coal in 40 cm³ of methanol and 0.1 cm³ of concentrated hydrochloric acid in a 100 cm³ round bottom flask and continuously stirring the coal/methanol slurry on a magnetic stirring plate for 3 hrs. The flask was connected to a cooling water condenser to reduce solvent losses by evaporation. Several experiments were completed in which dry nitrogen was used to blanket the coal/methanol slurry; elemental analyses of the treated coals showed no difference in the extent of oxidation when the system was purged with nitrogen and when it was vented to the atmosphere. Several blank experiments using hexane or acetone in place of methanol were also completed.

After pretreatment, most of the organic solvent was decanted off and the moist coal sample washed with three 50 cm³ aliquots of fresh solvent to remove residual acid. Any remaining solvent was recovered by roto-evaporation and vacuum drying (50° C, 10-20 millitorr pressure, 24 hrs.). Untreated coal samples were vacuum dried at the same conditions before liquefaction. After drying, all treated and untreated coal samples were stored at room temperature in a vacuum dessicator (0.1 torr) before analysis or liquefaction. Reactor runs were scheduled so that each coal sample was stored for less than 12 hours before use.

Liquefaction experiments were conducted in a 20 cm³ tubing bomb reactor attached to an agitator and immersed in a fluidized sandbath. Low severity reaction conditions were set at 350° C reaction temperature, 1000 psig initial cold hydrogen pressure, and 30 min. reaction time. Dihydro-phenanthrene (DHP) was used as hydrogen donor solvent (2/1 solvent/coal wt. ratio) in these runs. Coal conversion was measured using THF extraction data corrected for the intrinsic THF solubilities of treated and untreated coals. Solubility measurements were conducted at ambient conditions and consisted of three steps: 1) sonicating the liquid products from the tubing bomb reactor (or feed coal sample) in excess THF for 10 min., 2) centrifuging the mixture at 2000 rpm for 15 min., and 3) decanting THF-soluble products and excess THF from the THF-insoluble residuum. This procedure was repeated at least two times until no additional THF-soluble products were recovered. Remaining THF-insolubles were dried at 100° C for 24 hours to remove residual THF, weighed, and finally ashed. Coal conversion to THF-soluble products was computed as follows:

$$\text{Coal conversion} = \frac{M_f - M_p}{M_f} \times 100$$

(wt% maf basis)

where: M_f = mass of maf THF-insoluble coal charged

M_p = mass of maf THF-insoluble products recovered
(corrected to satisfy the ash balance)

RESULTS AND DISCUSSION

Baseline reactivity data for the untreated and treated Argonne coals are shown in Figures 1 and 2. Each of these data points represents the average of 2-3 reactor experiments. The average standard deviation for the dataset shown is ± 1.8 wt%.

At the low severity reaction conditions studied, three of the high volatile bituminous coals (Illinois #6 (72.1 wt%), Blind Canyon (69.6 wt%), and Pittsburgh #8 (57.0 wt%)) gave the highest THF conversions. Wyodak subbituminous coal was the next most reactive coal (44.4 wt%), while Pocahontas low volatile bituminous coal was the least reactive sample studied (15.6 wt%). These

reactivity data follow the same trends reported for the Argonne coals by several other investigators.

Pretreatment with methanol and HCl using the procedure described earlier enhanced low severity liquefaction reactivity for all eight Argonne coals. The absolute increase ranged from only 5.5 wt% for Blind Canyon coal to 31.5 wt% for Wyodak coal, and averaged 18.0 wt% for the eight coals. No simple trends in reactivity improvement with chemical or physical properties of the coals are obvious, although the reactivity of pretreated low rank coals (Wyodak and Beulah-Zap) increased much more than reactivity of the six bituminous coals.

Interestingly, replacement of methanol with hexane during coal pretreatment also enhanced low severity liquefaction reactivity. Since hexane cannot participate in the alkylation chemistry proposed by Sharma (7), other effects must also be contributing to the observed reactivity enhancement. Some possibilities include: 1) leaching of calcium, magnesium, iron, and perhaps other species from the coal mineral matter, and 2) formation of chlorinated mineral species such as FeCl_3 , which are known to be active coal dissolution catalysts (9,10). Other as yet unknown effects are certainly possible as well. Several additional sets of experiments and analyses are currently being conducted to begin elucidating the existence and importance of these effects.

Figure 3 compares the effect of our mild pretreatment method using methanol/HCl with low severity reactivity enhancement data for Wyodak coal samples alkylated using the Liotta (6) and Sternberg (5) alkylation techniques. As shown, our method provided a significant reactivity improvement even though the extent of alkylation was very low. These data also indicate that effects in addition to alkylation at oxygen and carbon sites in the organic coal structure are contributing to the observed improvements in coal liquefaction reactivity.

ACKNOWLEDGMENT

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Table I
Ultimate Analysis of Feed Coals

Wt% Dry Basis	Wyodak	Beulah-Zap	Illinois #6	Pittsburgh #8
Carbon	68.4	65.9	65.7	75.5
Hydrogen	4.9	4.4	4.2	4.8
Nitrogen	1.0	1.0	1.2	1.5
Sulfur	0.6	0.8	4.8	2.2
Oxygen	16.3	18.2	8.6	6.7
Ash	8.8	9.7	15.5	9.3
Coal Rank	Subbit.	Lignite	HVB	HVB
Symbol	Wy	BZ	Ill	Pit

Table I (cont.)
Ultimate Analysis of Feed Coals

Wt% Dry Basis	Blind Canyon	Lewiston-Stockton	Upper Freeport	Pocahontas
Carbon	76.9	66.2	74.2	86.7
Hydrogen	5.5	4.2	4.1	4.2
Nitrogen	1.5	1.3	1.4	1.3
Sulfur	0.6	0.7	2.3	0.7
Oxygen	10.8	7.8	4.8	2.3
Ash	4.7	19.8	13.2	4.8
Coal Rank	HVB	HVB	MVB	LVB
Symbol	BC	LS	UF	POC

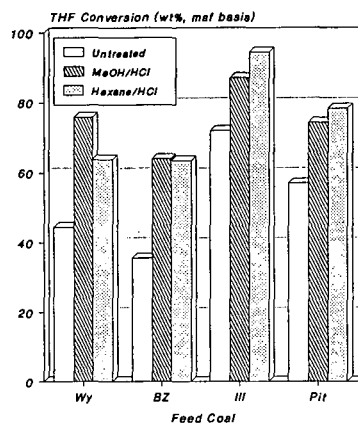


Figure 1. Effect of Pretreatment with MeOH/HCl and Hexane/HCl on Low Severity Liquefaction Reactivity of Argonne Coals

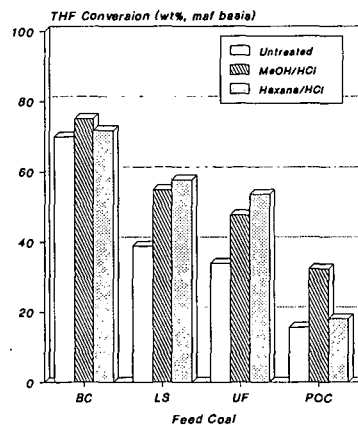


Figure 2. Effect of Pretreatment with MeOH/HCl and Hexane/HCl on Low Severity Liquefaction Reactivity of Argonne Coals

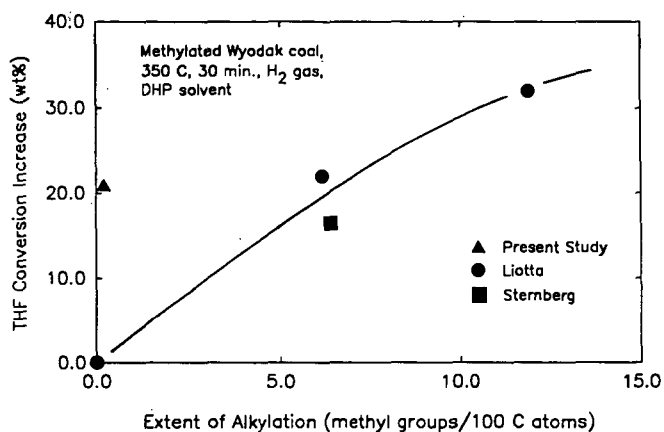


Figure 3. Liquefaction Reactivity Enhancement as a Function of Alkylation Extent for Three Pretreatment Methods

WATER PRETREATMENT OF COAL

Michael A. Serio, Peter R. Solomon, Erik Kroo, and Sylvie Charpenay

Advanced Fuel Research, Inc.
87 Church Street
East Hartford, CT 06108

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INTRODUCTION

Water pretreatment of coal has been studied previously as a means to increase the yields of liquid products from pyrolysis or liquefaction of coal. However, the mechanisms of this process and the applications to coals of a wide range of ranks are still a subject of considerable debate. Bienkowski et al. (1,2) have studied the effect of steam pretreatment on coal liquefaction. They used a Wyodak coal which had been carefully stored (under water) to avoid weathering. The experimental conditions were adjusted to provide 750 psig steam for 30 minutes in either a pretreatment (-200°C) stage and/or liquefaction stage. Pretreatment of the suction dried coal at 200°C increased the conversion to extractable products at 400°C from 30.5 to 38.5%. If the pretreatment was carried out at 240°C , the conversion was increased to 40.3%. However, increasing the pretreatment temperature even further to 320°C led to a smaller conversion (33.8%). In a later paper, Bienkowski et al. (2) tried ammonia addition to both reaction stages and obtained even better results than with steam alone.

The explanation offered by Bienkowski et al. (1,2) for the effect of steam pretreatment was that it allows breaking of hydrogen bonds, loosening of the coal matrix and stabilization of some of the reactive components of the coal. This effect appears to be enhanced by the presence of ammonia which can also provide hydrogen bonding and which may undergo chemical reactions with oxygen functional groups.

Graff and Brandes (3-5) have observed higher yields of liquid products from pyrolysis or solvent extractions of steam pretreated Illinois No. 6 coal. The steam pretreatment was done in a stainless steel microreactor at 50 atm (~ 750 psig) and $320\text{--}360^{\circ}\text{C}$. A similar pretreatment of coal in a helium atmosphere had no effect. If the steam-pretreated coal was exposed to air, both the improvements obtained in the pyrolysis and extraction yields were lost. The mechanism for the pretreatment was explained as partial depolymerization of the coal due to disruptions of hydrogen bonds. Recent evidence has suggested that the treatment increases the number of hydroxyl groups in the coal (5). It was postulated that the steam reacts with the ether linkages in coal, forming hydroxyl groups and reducing the number of covalent crosslinks in the coal (5).

Recent work by Khan et al. (6) involved the steam pretreatment of a set of five coals which covered a wide range of coal rank. The pretreatments were done at $300\text{--}320^{\circ}\text{C}$ and 1100-1300 psig steam. The steam pretreatment was found to reduce the concentration of oxygen functional groups for the low rank coals, but did not have much effect on higher rank coals (or increased the amount of oxygen). Under pyrolysis conditions, the low rank coals showed increases in tar yields, when pyrolyzed at a rapid rate. When the steam-treated coals were pyrolyzed at a slow heating rate, the tar yields did not increase significantly for any of the coals tested.

Ross et al. (7,8) have studied the liquefaction of Illinois No. 6 coal in $\text{CO}/\text{H}_2\text{O}$ systems at high pressure (4000-5000 psig) and high temperatures (400°C), where the water is supercritical. The conversion was measured in terms of toluene solubility (TS) and the results were found to be superior to those obtained in tetralin under the same conditions. The $\text{CO}/\text{H}_2\text{O}$ system was most effective (indicating a kinetic isotope effect) followed by $\text{CO}/\text{H}_2\text{O}$ and $\text{H}_2/\text{H}_2\text{O}$. The latter treatment was not very effective for demineralized coal. The results have been explained in terms of an ionic mechanism involving the initial formation of formate ion, as explained in Ref. 7, whereby hydrogen is donated to the coal.

Recent work by Ross and coworkers has addressed the use of liquid water as a pretreatment step to liquefaction in a conventional donor solvent (9,10). Work was done on Illinois No. 6 coal and

Wyodak subbituminous coal. The results did not show a significant effect of water pretreatment on increasing the conversion to toluene solubles in a donor liquefaction solvent. However, significant changes were observed in the composition and molecular weight distributions of the liquid products.

EXPERIMENTAL

Sample Selection

The selection of coal samples was made from the Argonne Premium Sample Bank. Since pretreatment is potentially most useful for lower rank coals which are subject to retrograde reactions, the coals selected were the Zap Lignite, the Wyodak subbituminous and the Illinois No. 6 bituminous, which are also being used in a complementary study (11). It is also planned to study coals which have been dried and/or aged, as there is evidence from the work of Graff and Brandes (3-5) and Bienkowski et al. (1,2) that the pretreatment is less effective on such coals, and that aging can reverse the beneficial effects of the pretreatment. The work to date has been done on the raw Zap and Wyodak coals.

Reactor for Steam/Water Pretreatment

A new reactor system was developed for this program, which is shown as a schematic in Fig. 1. This system was designed to carry out high pressure (up to 6000 psig), high temperature (up to -400°C) steam or water pretreatment of coal in a closed bomb reactor, which is also interchangeable with our current liquefaction reactor and product collection system. A schematic of the reactor is shown in Fig. 2. The inner volume of the bomb (20 ml) is divided into upper and lower parts by a stainless steel screen and glass wool. The screen is secured on the capillary tube and the glass wool is replaced after every experiment to keep the coal from being blown out on evacuation during the gas collection phase. After 1-3 g coal is fed into the bomb and the reactor head is screwed on to get a gas tight seal, the system is purged with N_2 or evacuated, the high temperature, high pressure valve on the reactor base is closed, and the water is injected directly into the coal through the capillary tube with a $\sim 0.1\text{-}1.0$ ml/min rate. Deaerated and deionized water is used throughout the reaction.

Simultaneously with the water injection, the reactor is immersed into the fluidized sand bath held at the required temperature. The pressure is measured in the water feed capillary tubing directly after the pump. The amount of water pumped in and the temperature determines whether steam and/or water pretreatment is done.

After the reaction, the bomb is quickly quenched with water, flooded with up to 300-600 psig N_2 , and depressurized with a 0.8 liter previously evacuated sampling tank. The yields of product gases, e.g., H_2 , CO_2 , CO , CH_4 , C_2H_6 , CH_2H_4 , CH_2H_2 , and H_2S are determined by GC. After opening the reactor, the pretreated coal is taken out of the reactor by washing it with deionized water and filtering under an N_2 atmosphere. N_2 was passed through the coal sample for about an hour to obtain a sample with approximately the same moisture content as the starting coal sample. In addition to the reactor, an N_2 purged glove box was also constructed to facilitate all the product work up in an oxygen-free environment. It is equipped with a lock which can be evacuated or filled with N_2 to transfer the reactor to the box.

RESULTS

An extensive series of steam pretreatment experiments was done on the Zap lignite using subcritical water at a pressure of 4000 psig and temperatures of 250, 300, and 350°C . Selected experiments were done for the Wyodak coal at 350°C , 4000 psig. The pretreatment times varied from 5 minutes to 5 hours. The pretreatment experiments with the Zap lignite over a wide range of temperatures and times give a fairly consistent picture based on analysis of the evolved gases during the pretreatment step and analysis of the solid residues by a variety of techniques (TG-FTIR, solvent extraction, FT-IR, x-ray, liquefaction). The TG-FTIR technique is a programmed pyrolysis instrument which includes on-line analysis of gases by FT-IR spectroscopy and on-line measurement of weight loss with a TGA (12,13).

The TG-FTIR analysis of residues produced at all three temperatures shows a sharp increase in tar at relatively short pretreatment times. The results for the tar yield for pretreatment at 350°C are shown in Fig. 3 for the Zap and in Fig. 4 for the Wyodak. The significant increase in tar does not persist at long pretreatment times. These changes are delayed and attenuated as the pretreatment temperature is reduced, as shown in Fig. 5 for the Zap lignite. However, there is a monotonic increase in the pyridine extractables (not shown) with increasing pretreatment time and a monotonic decrease in CO₂, as shown in Fig. 6 for the Zap lignite. The changes in the CO₂ evolution result primarily from changes in the organic CO₂, as shown by comparing Figs. 6a and 6b. The amount of CH₄ produced upon pyrolysis of the coal increased with increasing pretreatment time, as shown in Fig. 7. The results for the trends in the yields of tar, CH₄, CO₂ and pyridine extractables suggest that steam pretreatment is similar to a geological aging of the coal since these trends are nearly identical to the rank variations in these quantities. By this it is meant that the low rank Zap lignite exhibits behavior which is more characteristic of a higher rank coal after water pretreatment. This explanation is also consistent with the fact that the benefits of steam or water pretreatment are not observed for high rank coals (6). The similarity between the effects of steam pretreatment and geological aging has also been noted by Ross and coworkers (9,10). Landais and Monthieux have discussed the analogy between pyrolysis in confined systems and geological aging (14).

When liquefaction experiments are done on the steam pretreatment residues produced at 350°C, without shaking of the liquefaction reactor, no benefit to liquefaction yields is observed and, in fact, the yields are reduced. These results are shown in Fig. 8a. The liquefaction experiments were done in dihydrophenanthrene for 30 minutes at 400°C. A limited number of liquefaction experiments, which include shaking, have been done on the steam pretreated Zap residues produced at 350°C over a range of pretreatment times. These results are shown in Fig. 8b. These indicate a modest (10-20%) benefit to liquefaction yields at long pretreatment times (~ 5 hours).

An explanation for the effect of reactor shaking may be that the steam pretreatment process makes the coal agglomerate and thus more difficult to liquify. The agglomeration of coal by steam pretreatment was reported by Graff and Brandes (3-5) and Khan et al. (6) and has been observed in our own work.

Samples of residues from pretreatment experiments done at 350°C with Zap lignite were subjected to x-ray analysis. The results are summarized in Table 1, below.

TABLE 1
Effect of Water Pretreatment Time at 350°C, 4000 psig on Mineral
Compositions for Zap Lignite

Time (min)	Na	Ca	Al	S(o)	Ash
0	0.31	1.09	0.33	0.30	6.86
10	0.00	1.30	0.45	0.20	6.70
60	0.02	0.99	0.40	0.22	5.83
180	0.02	1.38	0.55	0.22	7.60
240	0.00	1.18	1.09	0.24	9.66

The total ash content was found to go through a minimum after about one hour pretreatment time and then increase with further increases in pretreatment time. This is in agreement with results obtained independently from a TGA combustion experiment, although the reasons for this are not yet clear. One possibility is segregation of the ash. For the individual ash components, the most significant trends were elimination of Na, and increases in Al, Si, and Fe with increased pretreatment time. The increases in Al and Fe may be due to partial dissolution of the reactor system. Little change was found for Mg, Ca, Ti, and organic sulfur.

Some of the residues from the 350°C experiments have also been analyzed by FT-IR. The preliminary results suggest that there is a reduction in oxygen functional groups during water pretreatment as was found by Khan et al. (6). Hopefully, the FT-IR results will allow us to verify some aspects of the chemistry of steam pretreatment which we suspect involves the interaction of H₂O, carboxyl groups and/or cations to produce methyl and hydroxyl groups. This is based on the fact that the beneficial effects of steam pretreatment are likely a result of a reduction in retrogressive reactions. Our previous work has suggested that carboxyl groups and cations are significantly involved in retrogressive reactions (15).

CONCLUSIONS

The preliminary conclusions are as follows:

1. The analysis of pyrolysis data from water pretreated Zap lignite (reduction in CO₂ yield, maximum in tar yield, increase in CH₄ yield, reduction in CO yield, maximum in extractables yields) shows a strong similarity to a geological aging process.
2. These changes are delayed and attenuated as the pretreatment temperature is reduced. The preliminary results for a Wyodak subbituminous coal are qualitatively similar.
3. The changes in the mineral composition due to water pretreatment are highly mineral specific.
4. Preliminary IR data is consistent with a general reduction of oxygen groups during water pretreatment.
5. The results from liquefaction experiments on samples produced to date indicate only modest benefits in donor solvent liquefaction.

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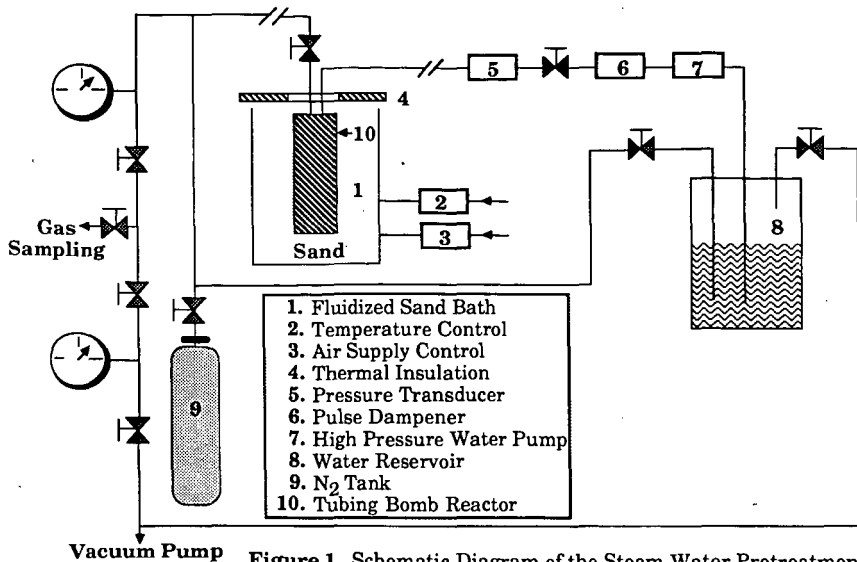


Figure 1. Schematic Diagram of the Steam-Water Pretreatment Reactor System.

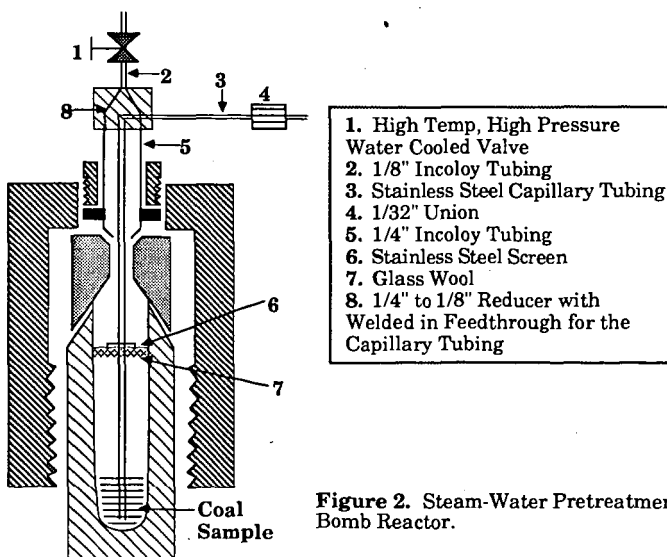


Figure 2. Steam-Water Pretreatment Bomb Reactor.

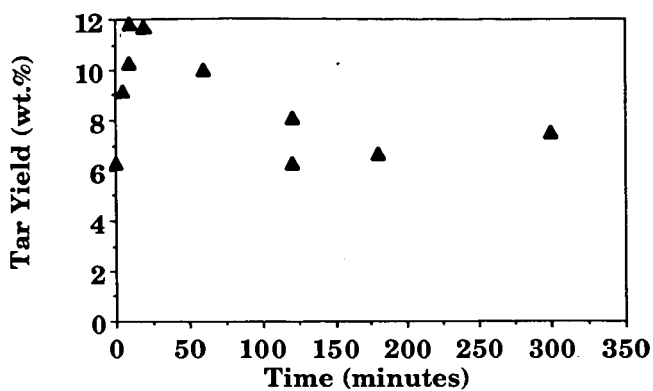


Figure 3. Tar Yield Data from Pyrolysis of Water Pretreated Zap Lignite (350°C, 4000 psig).

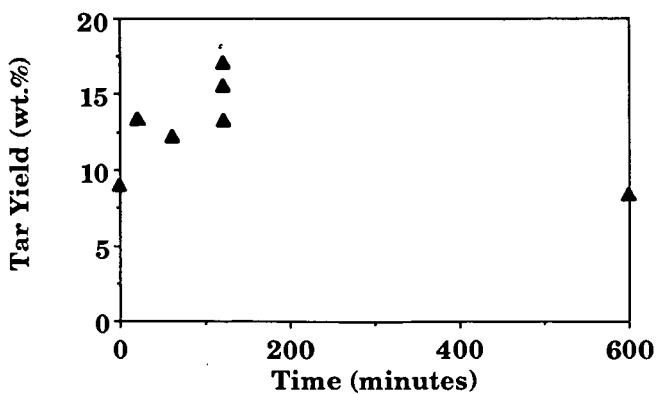


Figure 4. Tar Yield Data from Pyrolysis of Water Pretreated Wyodak Coal (350°C, 4000 psig).

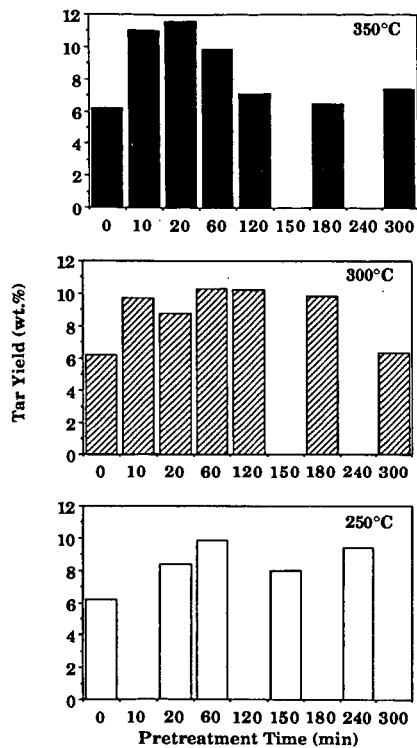


Figure 5. Tar Yield Data from Pyrolysis of Water Pretreated Zap Lignite Produced at Three Temperatures (4000 psig).

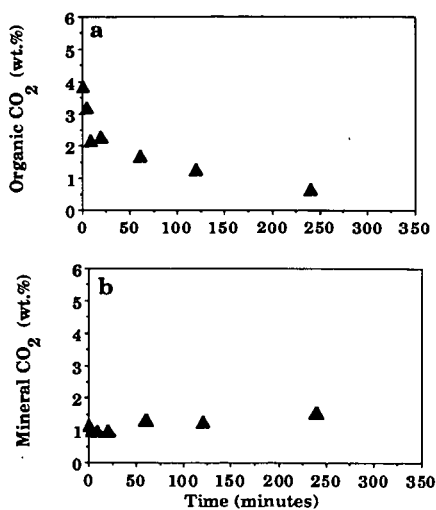


Figure 6. CO₂ Yield Data from Pyrolysis of Water Pretreated Zap Lignite (350°C, 4000 psig).

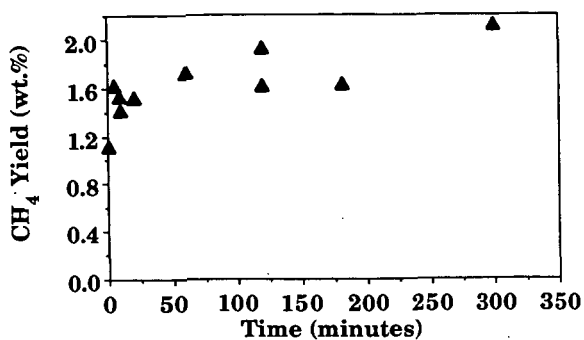


Figure 7. CH₄ Yield Data from Pyrolysis of Water Pretreated Zap Lignite (350°C, 4000 psig).

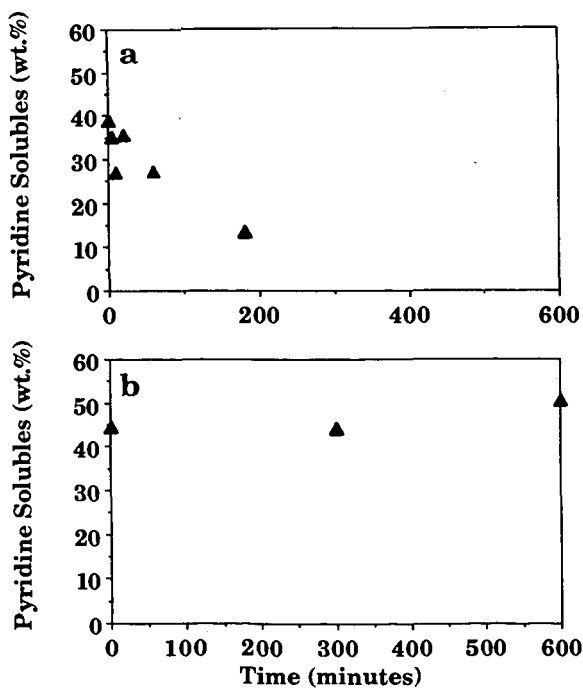


Figure 8. Pyridine Solubles Yields from Liquefaction Experiments with Water Pretreated Zap Lignite (350°C, 4000 psig).

Pretreatment for Coal Liquefaction

N. R. Pollack¹, G. D. Holder², and R. P. Warzinski

U.S. Department of Energy, Pittsburgh Energy Technology Center
Pittsburgh, PA 15236

Keywords: coal liquefaction, pretreatment, mass transfer limitations

Abstract

Pretreatment of Illinois No. 6 coal using two different procedures at moderate temperatures, 100°C to 300°C, resulted in small (up to 8%) but consistent increases in subsequent liquefaction yields. In a hydrothermal pretreatment, coal and water were heated together and then separated. The increase in yields due to this pretreatment are probably due to a chemical change in the coal. A method of modelling chemically effective pretreatments is proposed. The other pretreatment that increased liquefaction yields involved soaking the coal at 300°C in a coal-derived solvent prior to liquefaction. Particle size experiments were also performed to determine if mass-transfer resistance was a factor. At short contact times, liquefaction yields were greater with smaller particles, whereas, at longer contact times, the yields approached the same limiting value regardless of the initial coal particle size.

Introduction

The use of pretreatments, including catalyst dispersion, to enhance the liquefaction of coal has recently drawn considerable interest. Such pretreatments are proposed to open up the pores of the coal, provide a more intimate contact of catalyst and coal, and possibly affect the ultimate reaction chemistry by chemically altering the nature of coal prior to the liquefaction step. In this paper, such pretreatments will be classified into two types: Type I, which are those primarily aimed at reducing mass-transfer limitations between the coal and liquefaction media; and Type II, which are those designed to affect the liquefaction chemistry.

Examples of Type I pretreatments include those which open the pores of the coal allowing the solvent and hydrogen to more easily penetrate the coal particle or those in which a catalyst or other chemical, such as a hydrogen donor, is placed within the pores of the coal so that it is at the reaction site when liquefaction begins. Note that the process of catalyst deposition may affect the morphology of the catalyst and would need to be distinguished from mass-transfer-related effects. With the exception of catalyst morphology effects, all of these pretreatments are designed to overcome mass-transfer limitations. Type I pretreatments would therefore be ineffective if such limitations do not exist in the particular liquefaction scheme under investigation.

Only those pretreatments that produce a change in the chemical structure, surface properties, or molecular arrangement of the coal prior to liquefaction can be classified as Type II pretreatments. If the same effect can be produced by just adding the reagent(s) to the liquefaction step, then a separate pretreatment would not be necessary.

¹ Calgon Carbon Corporation, Robinson Township PA 15205

² University of Pittsburgh, Pittsburgh, PA 15216

For example, in order for a hydrothermal pretreatment to be judged a Type II pretreatment, the water must produce an effect that is different than would be obtained by just adding water to the liquefaction solvent. This concept is fundamental in evaluating any Type II pretreatment.

Background

During the past several years, coal pretreatments have received increased attention as a means of improving the liquefaction process by either lowering the reaction severity or improving yields under conventional liquefaction conditions. Examples of Type I pretreatments include solvent swelling or presoaking in the liquefaction solvent, both of which have been previously reported to enhance liquefaction yields (1,2,3,4). The most straightforward Type I pretreatment would be a reduction in particle size. This subject has been reviewed by Whitehurst et al. (5). They concluded that, while some variations in conversion were observed for different particle sizes, there were no significant mass-transfer limitations in coal liquefaction, especially when good hydrogen-donor solvents were used in well-agitated systems. In other processes, however, such as high-temperature solvent extraction (5,6) and for chemical reactions at temperatures below those used for conventional liquefaction (7), the presence of significant intraparticle mass-transfer limitations was sometimes observed. Since the presence of mass-transfer limitations is dependent on the type of process and on the mechanics of the system being used, it is therefore judicious to investigate this matter in the development of a Type I pretreatment.

Common Type II pretreatments used for coal liquefaction are alkylation and hydrothermal processing. A recent example of an alkylation pretreatment is the work by Baldwin et al. (8). In this work, mild O-alkylation was shown to be a beneficial pretreatment for a subbituminous coal. The benefit was associated with the suppression of cross-linking reactions that take place during the initial stages of coal thermolysis. The effects were most pronounced at lower reaction severity. Concerning hydrothermal pretreatments, improvements in pyrolysis conversions resulting from steam and hot water pretreatments were originally reported by Brandes et al. (9), and Bienkowski et al. (10). Mochida also reported an improvement in liquefaction yields in a pyrene solvent system associated with a boiling-water pretreatment (11). Ross and coworkers report some improvement in product quality from donor-solvent liquefaction of a hydrothermally pretreated coal (12). Although these various systems have been studied, the mechanism and the actual benefit of hydrothermal pretreatments in liquefaction systems are still not fully understood.

Experimental

Two samples of Illinois No. 6 coal were used in the work reported here. Elemental analyses are contained in Table 1. One sample was ground to minus 48-mesh and minus 325-mesh top sizes. From a second sample of lump-size coal, a 10x48 mesh fraction was screened out after passing the coal through a delumper and a jaw mill. Part of the 10x48 fraction was further ground in a ball mill for 15 minutes under argon to produce a minus 230-mesh sample. The coal-derived liquefaction solvent was a hydrogenated heavy distillate obtained from the V1074 separator at the Advanced Coal Liquefaction Test Facility in Wilsonville, Alabama.

A 38 cm³ (2.54-cm o.d., 12.7-cm long) stainless-steel microautoclave was used to perform the high-temperature pretreatments and the liquefaction tests. During operation, the microautoclave is

horizontally positioned and agitated by a Burrell wrist-action shaker. The microautoclave is rapidly heated to reaction temperature by immersion in a hot sand bath and quenched after reaction in water. Zero-contact-time experiments involved quenching the microautoclave as soon as reaction temperature was attained. The internal temperature and pressure are continuously monitored.

The liquefaction tests were performed on 3 g of coal or treated coal that was mixed with 9 g of solvent in the microautoclave. A 1000 psig hydrogen or nitrogen cold charge was used in these tests. Liquefaction conversions are measured by methylene chloride and n-heptane solubility and are based on the dry, ash-free, insoluble residues. The standard error in the conversion determinations is less than 4% in both cases. Additional details are available elsewhere (13, 14).

The hydrothermal pretreatments were performed using 5 g of coal and 10 g of water under an initial nitrogen pressure of 500 psig. After 30 minutes at 300°C, the microautoclave was quenched and transferred to a nitrogen-filled glove box where it was vented and opened. The contents were removed with deionized water and filtered to remove the excess water. A portion of the sample was then placed back in the microautoclave for the liquefaction test. Another portion was analyzed to determine the moisture and ash content of the pretreated sample.

In the presoak pretreatments, the microautoclave was heated to 300°C for 10 minutes before being transferred to another sandbath that was preheated to liquefaction temperatures. In one case, the presoak pretreatment was performed by placing the microautoclave and its contents in a cold sandbath and gradually bringing it up to liquefaction temperature over a period of about 2 hours.

Results and Discussion

Results of a Type I pretreatment on the minus 48-mesh sample of Illinois No. 6 coal are shown in Figure 1. The pretreatment involved presoaking the coal in the Wilsonville V1074 recycle solvent prior to liquefaction. In one case, indicated by PS in Figure 1, the presoak was carried out at 300°C for 10 minutes prior to immersing the reactor in another sand bath at liquefaction temperature. In another case, indicated by SH in Figure 1, the microautoclave was slowly heated to reaction temperature over a period of about 2 hours. At 400°C, both presoaking and slow heating led to small increases in conversion to both methylene-chloride and n-heptane solubles. The increases were less for the longer experiment in which slower heating was used. The magnitudes of the observed increases were of the same order of magnitude as that observed by Narain (4) but less than those observed by others (1,3).

Figure 1 also shows that increasing the liquefaction temperature to 425°C results in the pretreatment effect being absent in the case of the n-heptane conversions and negative for the conversions measured with methylene chloride. These results represent part of a larger body of experimental data yet to be reported (13), but they serve to illustrate the sensitivity we observed for this type of pretreatment with respect to the actual liquefaction conditions used.

To further assess the role of mass transfer limitations in donor-solvent liquefaction, experiments with Illinois No. 6 coal of various mesh sizes were conducted. Results of using these fractions in the Wilsonville V1074 solvent system are shown in Figure 2. Any benefits of using the smaller particle sizes in this system are only observed at very short contact times and diminish as contact time increases. As

with the presoak results described above, liquefaction at 425°C diminishes any benefit observed at the lower temperature.

Another set of experiments on this subject was performed to isolate the effect of solvent/coal contact using the more carefully sized coal particles (see the Experimental section for details). The liquefaction tests in this case were conducted at 400°C in tetralin under an inert atmosphere. As before, the results, contained in Figure 3, show that a small but consistent increase in methylene-chloride and n-heptane conversions accompany the use of the smaller-sized particles. The magnitude of the increase diminishes with increasing contact time but is still evident at 20 minutes. Analysis of the methylene-chloride-insoluble product produced from the 10X48 mesh sample showed the presence of particles larger than 48 mesh for the 0 and 5 minute tests but no evidence of the original particles at 20 minutes.

In summary of the above, the small influence that initial particle size has on ultimate (longer contact time) yields indicates that the same asymptotic yields are reached although the initial conversion is moderately inhibited by the larger particles. The asymptotic behavior also implies that the reactions are delayed slightly but not significantly changed in nature. The results from these tests and the presoak experiments indicate that mass-transfer limitations may exist under certain conditions and that, in these cases, Type I pretreatments may be effective in reducing these limitations. However, under conventional liquefaction conditions, large benefits should not be expected from Type I pretreatments. Such pretreatments may have greater utility under lower-severity conditions where coal particles do not disintegrate rapidly and the rates of the liquefaction reactions are slower. The work described here indicates that the largest effect related to any mass-transfer limitations probably occurs during the initial heating to liquefaction temperatures, since only small improvements are observed even in zero-contact-time experiments.

The effect of using a hydrothermal (Type II) pretreatment on Illinois No. 6 coal is shown in Figure 4. The pretreatments resulted in a small but consistent improvement in the methylene-chloride solubles (2%) and the heptane solubles (6%) compared to the yields obtained for untreated coals. In other work, similar but less consistent results were obtained for a Wyodak coal (13). These results are consistent with those of Ross and coworkers (12), which show similar small improvements in the yields of toluene soluble material after a hydrothermal pretreatment at 250°C. They also noted an improvement in the product quality due to the pretreatment as determined from FIMS data. They postulate that the pretreatment disrupts chemical associations between the organic and mineral phases of the coal causing the release of organic matter. In other work, Mochida et al. (11) speculate that hydrothermal pretreatments remove divalent cations such as Ca^{2+} and Mg^{2+} , which link oxygen functionalities and thereby impede liquefaction. In the pyrolysis work of Brandes et al. (9), the proposed reason for increased yields is the chemical interaction of the steam used in the pretreatment with oxygen functional groups in the coal. Although the hypothesized mechanisms for hydrothermal pretreatment are varied, the consensus is that it is a chemical effect and therefore classified as a Type II pretreatment. Also, in previous work, the addition of water directly to the liquefaction reactor was not found to cause any benefit in the conversion results or product quality (12,14).

The primary way by which Type II pretreatments can affect the degree of conversion as measured by solvent solubility is to change the rate at which soluble and/or insoluble products are produced. To be effective, the pretreatment must accelerate the rate at which soluble products are

produced, in the same manner that a catalyst would, or decelerate the rate at which insoluble products are produced. A simple first-order model can be used to describe the production of soluble and insoluble products from coal:

Coal $\xrightarrow{k_s}$ Soluble Products

Coal $\xrightarrow{k_I}$ Insoluble Products

where k_s and k_I represent the rate constants for the reactions indicated. Using the first-order models, it is possible to determine the relative rate constants, k_s/k_I , before and after pretreatment by solving the following equation.

$$k_s + k_I = -\ln[1 - x_s(1 + k_I/k_s)]/t$$

where x_s is the fractional conversion to solubles at time t . Since two unknowns are present, conversions must be available at more than one reaction time. It should be noted that the k_s/k_I ratio would remain the same if both rates changed by the same amount (if the pretreatment caused the same final state to be reached only at a different time). Also note that the model does not explicitly account for the production of gases.

For the hydrothermal pretreatments shown in Figure 4, the k_s/k_I ratio for the methylene-chloride-soluble products improves from 1.47 prior to pretreatment to 1.61 after pretreatment. This small increase could be due either to an increase in the rate of formation of soluble products or to a decrease in the rate of formation of insoluble products.

The ratio, k_s/k_I , has been calculated for other chemical pretreatments reported in the literature. For hydrothermal pretreatment of oxidized coal prior to liquefaction in an aqueous-KOH/CO system (14), k_s/k_I for methylene-chloride-soluble products increased from 0.37 to 1.82. Alkylation of Wyodak Coal prior to donor-solvent liquefaction (8) caused the ratio for tetrahydrofuran-soluble products to increase from 0.54 to 2.22. Comparing these values with the ratio calculated for the experiments in Figure 4 shows that hydrothermal pretreatment prior to donor-solvent liquefaction has a smaller effect than the other pretreatments and liquefaction systems mentioned. Note that the largest effect of pretreatment comes when the initial ratio of k_s/k_I is quite small (0.4 to 0.5) owing either to a low rate of formation of soluble products or a high rate of formation of insoluble products.

Conclusions

The results of the experiments reported in this paper show that presoaking (a Type I pretreatment) in the liquefaction solvent resulted in small but consistent increases in conversions in a donor-solvent liquefaction system at temperatures below 425°C. Additional tests with different particle sizes confirmed the existence of mass-transfer limitations in the early stages of liquefaction under similar conditions. Overall, the benefit of using a Type I pretreatment will depend on the mass-transfer limitations relative to liquefaction rates in the system of interest. The greatest utility of Type I pretreatments will likely be in the development of lower-severity processes in which mass-transfer limitations would be greater and liquefaction rates lower. The effect of Type I pretreatments in catalytic systems also needs further investigation.

A Type II, hydrothermal pretreatment, also resulted in small but consistent increases in conversion in a donor-solvent liquefaction system. Other Type II pretreatments reported in the literature, such as alkylation, provide a greater benefit. A simple first-order model was used to compare the relative effectiveness of these Type II pretreatments. It is also important to note that benefits from Type II pretreatments can be due to an increase in formation of soluble products and/or to a reduction in the formation of insoluble products. These considerations should be taken into account when investigating Type II pretreatments.

Disclaimer

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Table 1. Elemental Analyses of Illinois No. 6 Coals Used.

Sample Designation	Moisture	Ash	----moisture and ash free----				
			C	H	O	N	S
-48 mesh	7.2	23.1	78.0	5.3	9.0	1.5	6.2
-325 mesh	5.2	22.9	77.3	5.3	9.7	1.5	6.1
10X48 mesh	9.5	16.2	83.2	4.8	5.2	1.5	5.4
-230 mesh	5.8	16.6	81.0	4.5	7.6	1.5	5.4

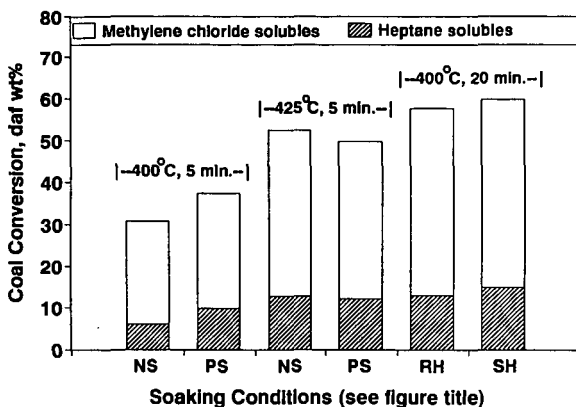


Figure 1. Effect of thermal soaking on the conversion of Illinois No. 6 coal in Wilsonville V1074 solvent. Liquefaction times and temperatures shown in the graph. All tests were under 1000 psig H_2 cold pressure. (NS - No Soaking, PS - Presoaked at 300°C for 10 min., RH - Rapid Heating, SH - Slow Heating)

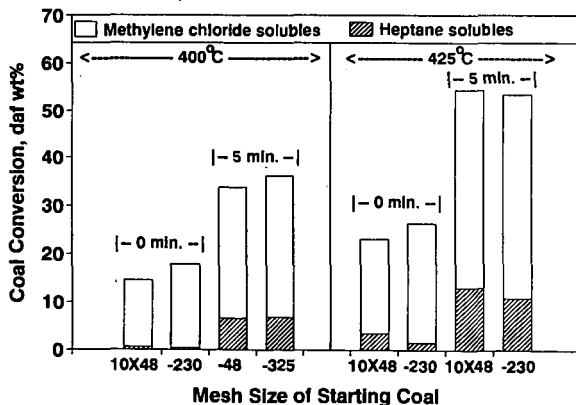


Figure 2. Effect of particle size on the conversion of Illinois No. 6 coal in Wilsonville V1074 solvent. Reaction times and temperatures shown in graph. All tests were under 1000 psig H_2 cold pressure.

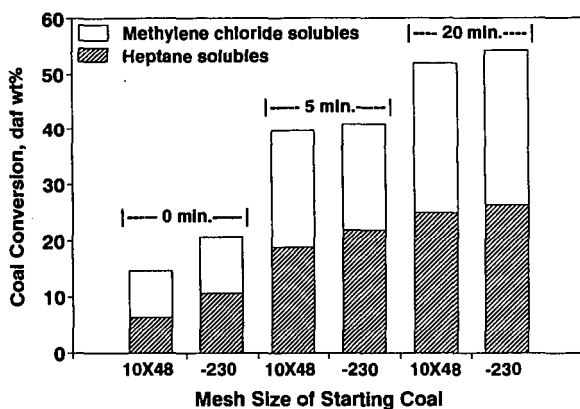


Figure 3. Effect of particle size on the conversion of Illinois No. 6 coal at 400°C for various times at reaction temperature. All tests were performed in tetralin under 1000 psig nitrogen cold pressure.

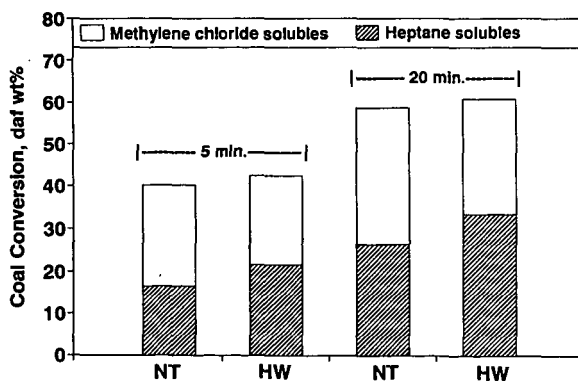


Figure 4. Effect of hydrothermal pretreatments on the conversion of Illinois No. 6 coal in tetralin at 400°C under 1000 psig (cold) H₂. NT - No treatment, HW - 15 minute pretreatment at 300°C under 500 psig (cold) N₂.

EFFECT OF HYDROTHERMAL PRETREATMENT FOR COPROCESSING

Doris S. Tse, Albert S. Hirschon, Ripudaman Malhotra, Donald F. McMillen, and David S. Ross

Chemistry Laboratory
SRI International Menlo Park, California 94025-3493

KEYWORDS: Water, Pretreatment, Coprocessing

ABSTRACT

We report here effects of hydrothermal pretreatment on coprocessing of three different coals from the Argonne Premium Coal Sample Program. Aqueous pretreatment has resulted in a marked beneficial effect in terms of conversion to hexane solubles for Wyodak subbituminous coal and Zap lignite. The effect on the Illinois No. 6 coal was negligible to slightly detrimental. Hydrothermal pretreatment of Wyodak subbituminous coal (1 part) at 250°, 300°, and 350°C for 30 min followed by coprocessing with Maya ATB (2 parts) at 425°C for 1 h, resulted in 26.0%, 23.5%, and 23.5% hexane insolubles based on total feed. Without hydrothermal pretreatment, 31.5% of the feed ended up as hexane insolubles. Use of a donor solvent, tetralin, in place of water during pretreatment produced 27.5% hexane insolubles, and thus was not as effective as hydrothermal pretreatment for the Wyodak coal. Coupling of phenolic constituents and the effect of water in minimizing such retrogressive reactions provide a possible explanation of these results. Support for this hypothesis was found in model compound studies with catechol. We observed that while coupling of catechol on kaolin proceeds very rapidly such that after 3 h at 350°C only 38% of the catechol was recovered, addition of water dramatically mitigated the coupling, with 96% recovery.

INTRODUCTION

The impact of water on coal conversion under different process conditions has been a subject of interest and controversy for some time. Recent studies have shown that mild hydrothermal treatment of an Illinois No. 6 coal substantially enhances conversion into soluble products. For instance the convertibility of an Illinois No. 6 coal into toluene-soluble products increased from ~ 35% to almost 70% when the coal was treated for 30 minutes with water at 250°C under nitrogen, and then subjected to conversion in CO/water systems.⁽¹⁾ Similar favorable effects of mild hydrothermal pretreatment have also been reported for conversions in pyrene ⁽²⁾ and for rapid hydropyrolysis.^(3,4) However, the benefits of water pretreatment are clearly not general in that they are not observed for all coals under all combinations of pretreatment and subsequent processing conditions.

We present here results from a study we undertook to determine whether the beneficial effects of mild hydrothermal pretreatment can be exploited in the context of coprocessing. The objectives of this study were to explore the range of benefits, with respect to coal type, temperature of pretreatment, and the manner of water removal. In a parallel study, we have examined the impact of water on clay-catalyzed coupling of phenolics. Together, the two studies strongly indicate that the beneficial impact of water is due to the suppression of retrogressive coupling reactions.

EXPERIMENTAL

The coals used in this study were Wyodak-Anderson seam subbituminous coal, Illinois No. 6 seam high volatile bituminous coal, and Beulah-Zap seam North Dakota lignite; all coals were obtained from the Argonne premium coal bank and used as received. To minimize exposure to air and the time between pretreatment and coprocessing, both the steps were conducted in the same microautoclave. The reactor (43 mL) was charged with approximately 2.25 g of the coal and subjected to pretreatment conditions. Aqueous pretreatment was conducted at 250°, 300°, or 350°C for 0.5 h. After cooling, the excess water was pipetted out. Approximately 4.5 g of Maya ATB was added to the reactor, which was then filled with 1200 psig of hydrogen (cold). The reactor was shaken at 425°C for 1 h in a fluidized sandbath. Before opening the reactor, it was cooled in dry ice to prevent volatiles from escaping. Conversion to hexane solubles was the principal diagnostic used in this study, although other parameters such as THF-solubles, elemental composition, and FIMS-volatility were also determined for selected cases.

RESULTS AND DISCUSSION

Table 1 presents data from the coprocessing studies with Argonne premium samples of Wyodak coal and Maya ATB for a variety of pretreatment conditions. Experiment 1 in Table 1 gives conversion of Maya alone with no coal added and Experiment 2 gives the result for coprocessing without any pretreatment. These entries represent base-line values to be used for determining the effect of various pretreatments shown in subsequent lines. Using the baseline conversion of Maya alone, we can determine the theoretical conversions of coal assuming that there is no interaction between the coal and the resid. For instance, 18% by weight of hexane insoluble (HI) material was obtained after treating Maya under these thermal coprocessing conditions. If coal were added (in a ratio of 1 part coal to 2 parts Maya), then we would have obtained a yield of 12% if all of the coal had been converted to hexane soluble material. In contrast, if none of the coal had been converted, a value of 45% insoluble material would have been obtained. As shown in the table the results ranged from 22 to 34% hexane insoluble material, indicating that a significant portion of the coal had been converted.

Effect of Pretreatment Conditions on Coprocessing of Wyodak and Maya ATB

From the data in Table 1 we can immediately see that there is a marked beneficial impact of hydrothermal pretreatment with the yield of hexane-insolubles being reduced from 32% without pretreatment to 26% with pretreatment at 250°C (Experiments 3 and 4). Hydrothermal pretreatment at 300°C further reduces hexane-insolubles yield to 24%. Increasing the pretreatment temperature to 350°C results in no further benefit in terms of conversion to hexane-solubles. The additional conversion is not merely due to the extra heating that pretreatment provides. Dry heating of coal for 30 min at 350°C prior to coprocessing is in fact deleterious and results in 34% hexane-insolubles. Even thermal pretreatment in tetralin, a donor solvent, is not as beneficial as hydrothermal pretreatment.

Baldwin et al. have shown that mild pretreatment treatment of several coals with acidic alcohol solutions results in enhanced conversion during subsequent coprocessing.⁽⁵⁾ The premise of their work was that the pretreatment alkylates the coals thus preventing the phenolic and carboxylic groups from undergoing retrogressive reactions and lowering the yields. However, another possibility is that the pretreatment actually dewatered the coal, and the removal of water under mild conditions aided in the enhanced conversions. To test this hypothesis we used acetone which is also completely miscible with water, but which cannot alkylate hydroxyls. However, this treatment was somewhat deleterious and resulted in a slight increase in hexane-insolubles: 34% compared to the base line case of 33%.

To determine if the pretreatment effect was limited to the coal, we treated the Maya ATB at 350°C in water. The water was removed, and Maya ATB was then subjected to treatment at 425°C in nitrogen (Experiment 15) and in hydrogen (Experiment 16). In both cases the conversion was no different from that of no pretreatment. The fact that the HI yields under nitrogen and hydrogen for pure Maya are the same is interesting, and suggests that perhaps the upgrading of the Maya is

primarily a disproportionation reaction, where the hydrogen utilized for the upgrading comes directly from the Maya ATB itself. This conclusion is in concert with the findings of Savage et al., (6) and Khorasheh et al. (7) who have reported that presence of hydrogen does not increase the yield of the distillates (which is often equated to hexane-solubles) under thermal and catalytic processing of resids and gas oils, although it reduces coke formation.

Effect of Coal Rank on Hydrothermal Pretreatment

Table 2 presents data from the coprocessing studies with Argonne premium samples of Wyodak, Illinois No. 6, and North Dakota coals and lignite. Although bituminous coals are generally more easily converted than subbituminous coals, coprocessing of Wyodak and Illinois No. 6 coals without pretreatment led to about the same extent of conversion, yielding 32-34% hexane-insoluble material. However, although the pretreatment of Wyodak gave a significant enhancement of conversion, no benefit for the Illinois No. 6 coal was observed. Hydrothermal pretreatment of the lignite at 350°C was moderately beneficial. It should be remembered that we had optimized the pretreatment conditions using the Wyodak coal; and *a priori* have no reason to assume that these conditions are optimal for other coals as well. The lignite may show a more pronounced effect with a lower temperature hydrothermal pretreatment. Nevertheless, these results show that the beneficial effects of hydrothermal pretreatment are not specific to the Wyodak coal and that other low rank coals also show qualitatively similar enhancement in conversion.

Possible Chemical Basis for Hydrothermal Pretreatment

Various factors could explain the phenomenon of hydrothermal pretreatment and how it relates to the ultimate convertibility of coal. One possibility is that morphological changes affect mass transfer rates because the water contact increases pore volume and therefore opens the coal structure for subsequent conversions. However, other, more chemical explanations must also be considered. Because the impact of hydrothermal pretreatment was generally more pronounced for low rank coals, which have relatively large amount of dihydric phenols, and because dihydric phenols are particularly prone to coupling reactions, we investigated the effects of mineral/organic interactions by use of model phenol systems such as phenol and catechol, and mineral systems such as montmorillonite and kaolinite. In previous work we have shown that unless H-donor solvents are present, phenolics such as catechol and resorcinol undergo rapid coupling reactions (8). Trewheella et al., have also reported that the presence of hydrogen donors such as tetralin significantly reduces the polymerization of phenolic compounds to larger ring furans (9).

We conducted a series of experiments in which catechol was heated in a sealed quartz ampoule in the presence of kaolin, a common clay mineral found in coals, and in the presence or absence of water or tetralin. Under the experimental conditions a substantial amount of catechol was converted to polymeric materials and not recovered. The product mixture was analyzed by GCMS to determine the amount of unconverted catechol and the small yields of phenol. Table 3 presents data on the self-coupling reactions of catechol in the temperature range from 300° to 400°C, and how it is modified by kaolin, tetralin, and water. As shown in this table, only a small amount of the catechol underwent any condensation reactions when heated by itself to 400°C for 1 h (Experiment 1). It remained essentially as catechol (75%) or phenol (18%) with only 7% of material unaccounted for. Reaction at 350°C (Experiment 4) results in even less of coupling products. However addition of kaolin markedly accelerated coupling reactions. For instance, after 3 h at 350°C a mixture of catechol and kaolin (Experiment 5) contains only 46% of the original catechol (and 4% phenol), compared to 92% and 1% with no clay added (Experiment 4). Addition of water, on the other hand, results in inhibition of these coupling reactions. In Experiment 6 water was added to the mixture, and 89% of the catechol was recovered, and 1% phenol was formed. Analogous effects of clay and water were observed at 400°C. Addition of clay promotes coupling of catechol with only 2% of the catechol being recovered (Experiment 2), while in the presence of water, 84% was recovered (Experiment 3). These results are very interesting, and suggest that pretreatments and/or conversions in the presence of water should minimize crosslink formation by phenols of this type and lead to larger yield and/or a better quality product.

CONCLUSIONS

We have shown here that hydrothermal pretreatment of low rank coals enhances conversion to hexane-solubles during subsequent coprocessing. We further showed that for the Wyodak coal, the benefit increased from an increase in the pretreatment temperature from 250° to 300°C, but no additional benefits were derived by further increase of temperature to 300°C. Dry thermal pretreatment is detrimental and even thermal pretreatment in donor solvents is not as effective as aqueous pretreatment. We suspect that some of the benefits seen here evolve from changes brought about in clay-promoted retrogressive condensation chemistry. In a small study conducted to understand this phenomena we have shown that water markedly attenuates the clay-catalyzed coupling of phenolics.

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Table 1

**COAL CONVERSION FROM COPROCESSING MAYA ATB AND WYODAK
COAL IN MICROAUTOCLAVE^a**

Experiment	Pretreatment ^b	HI (wt%)	Coal Conversion ^b
1	Maya (no coal)	18	--
2	None	32	40
3	250 °C	26	53
4	250 °C	27	53
5	300°C	23	66
6	300°C	24	63
7	350°C	22	69
8	350°C	25	60
9	Thermal 350°C	34	33
10	Thermal 350°C	34	33
11	Vac Dried 56°C	34	33
12	Acetone Dried	33	36
13	Tetralin 350°C	28	52
14	Tetralin 350°C	27	55
15	Maya (no coal, 350 pret)	20	--
16	Maya (no coal, 350 pret)	23	--

a. Reactions of coal and Maya ATB at 425°C for 1 h at and 1200 psi H₂. HI refers to Hexane insoluble fractions.

b. Coal conversion calculated assuming that the insoluble material from the Maya remains the same during the coprocessing experiment.

Table 2
COPROCESSING OF COALS OF DIFFERENT RANK WITH MAYA ATB IN
MICROAUTOCLAVE^a

Experiment	Coal	Pretreatment	Hexane Insoluble	Coal Conversion ^b
1	None	None	18	--
2	Wyodak	None	32	40
3	Wyodak	350°C	22	69
4	Wyodak	350°C	25	61
5	Illinois No. 6	None	34	33
6	Illinois No. 6	350°C	35	30
7	Lignite	None	28	52
8	Lignite	350°C	24	64

a. Reactions of coal and Maya ATB at 425°C for 1 h at and 1200 psi H₂.

b. Coal conversion calculated assuming that the insoluble material from the Maya remains the same during the coprocessing experiment.

Table 3.
EFFECT OF WATER ON CLAY-CATALYZED COUPLING REACTIONS OF
CATECHOL

Run	Description	Temp (°C)	Time (h)	Mass Balance (Mol%)		
				Catechol	Phenol	Remainder
1	Catechol	400	1	75	18	7
2	Catechol/ Kaolin	400	1	2	0.2	98
3	Catechol/ Kaolin/water	400	1	84	3	13
4	Catechol	350	3	92	1	7
5	Catechol/ Kaolin	350	3	38	4	52
6	Catechol/ Kaolin/water	350	3	89	1	10
7	Catechol/ Kaolin	300	5	83	8	9
8	Catechol/ Kaolin/water	300	5	99	0	0

LOW TEMPERATURE SWELLING OF ARGONNE PREMIUM COAL SAMPLES: EFFECT ON PORE STRUCTURE

Dennis R. Spears, Lowell D. Kispert and Lidia Piekara-Sady

Box 870336, Chemistry Department,
The University of Alabama, Tuscaloosa, AL 35487-0336

ABSTRACT

Changes in the pore structure of Argonne Premium Coal Samples (APCS) upon slurrying at different temperatures with the solvents toluene, nitrobenzene and pyridine were followed using an EPR spin probe method. At room temperature, spherical shaped pores in coal slurried with nitrobenzene become elongated and cylindrical at 60°C. Coal slurried with pyridine exhibits few detectable spherical shaped pores at room temperature but exhibits significant concentrations of elongated pores at 60°C. This change in pore structure was attributed to the break-up of the hydrogen bonding network by the pyridine solvent.

INTRODUCTION

The organic portion of coal consists of an entangled, extensively cross-linked network of high-molecular weight subunits. The subunits vary in composition and are cross-linked by both covalent and hydrogen-bonding linkages (1). The network, although polymeric in nature, is still not well understood. Adding to the difficulties in understanding coal structure is the porous nature of coal (2). Guest molecules of varying molecular weight are trapped within the network and within the pore system (3). Because coal is polymeric in nature, classical solvent swelling techniques have been used to better understand the structure of coal.

Solvent swelling of coal is important for several reasons. Solvent swelling studies have been used to estimate the average molecular weight between crosslinks (4), and to understand the bonding between subunits (5,6). Understanding solvent swelling is important because organic solvents affect the pore structure of coal, as well as density, mechanical strength, and spectral properties. Further, many coal beneficiation processes, especially liquefaction, take place in organic solvents.

The pore structure of coal has been extensively characterized (7,8). Swelling solvents act upon coal via diffusion into the pore structure. Catalysts can penetrate into accessible areas during conversion processes. Among the many techniques used to characterize the pore structure of coal has been the use of spin probes and electron paramagnetic resonance spectroscopy (EPR) (9-16).

Until the early part of this decade, EPR was used primarily to study the concentration of free radicals in coal and determine g-values. However, in 1981 Silbernagel et al. (9) showed the possibility of diffusing spin probes into coal as observed by EPR spectroscopy. TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) was placed in a hexane solution and diffused into either Wyodak or Illinois No. 6 coal. The broadening and reduction of the nitroxide spin probe EPR signal was associated with the diffusion of the TEMPOL molecules into the coal matrix. This experiment suggested that surface adsorption and diffusion of spin probes into coal was possible (9).

This method has been expanded in our laboratory (10). EPR studies of doped Alabama and Penn State Coal Sample Bank (PSOC) coals were carried out, showing it possible to estimate the relative accessibility of different sized spin probes to the pore structure of coals in the presence of a swelling solvent (10-16). Spin probes of different sizes and shapes are diffused into different coal samples swelled with toluene. A nonswelling solvent such as cyclohexane is used to wash away the spin probes not trapped in the porous structure. Relative pore shapes and size distributions can then be

determined by EPR measurement of the spin concentration of the probes trapped within the matrix. In this paper, changes in both pore size and shape with coal rank and swelling solvent were determined as a function of swelling temperature for the Argonne Premium Coal Samples (APCS).

EXPERIMENTAL

All eight Argonne premium coal samples were used in this study. The compositions of these coals on a dry, mineral matter-free basis are shown in Table 1. The coals were doped with spin probes using a procedure described previously (13-16). The coals were swelled with either toluene, nitrobenzene or pyridine solutions of the desired spin probes. This paper details the results of the spin probe commonly known as TEMPOL, I, spin probe V (4-octadecanoylamino-2,2,6,6-tetramethylpiperidine-1-oxyl) and spin probe XIII (4-nonylamino-2,2,6,6-tetramethylpiperidine-1-oxyl). The structures of these probes are given in Figure 1. I was obtained from Aldrich and V and XIII were obtained from Molecular Probes. Spin probe I is roughly spherical in shape while probes XIII and V are elongated. The coals were swelled either at room temperature or at 333 K.

RESULTS AND DISCUSSION

The ability of a solvent to swell a given coal depends upon many factors, including the polarity of the solvent, temperature of solvolysis and rank of the coal. The swelling conditions used in this study were fairly mild. At room temperature with n-alkyl amine solvents, equilibrium swelling ratios require weeks to reach (17). The intention in this study was not to reach swelling equilibrium but rather an equilibrium uptake of the spin probe. This was found to occur after 12 hours.

Nonpolar solvents interact with coal in accordance with regular solution theory; polar solvents swell coal by disrupting hydrogen bonds. Coal is cross-linked with both covalent and hydrogen-bond cross-links. Hydrogen bonding is especially important for lower rank coals, but diminishes in importance with rank (5). Hydrogen bonding is believed to be associated with oxygen functionalities (18), and the oxygen content of coal decreases with rank. Thus, polar solvents show a lessened ability to swell higher ranked coals. Further, the degree of solvent polarity affects the ability of a solvent to disrupt hydrogen bonds and swell coal (19). Swellability also decreases with rank for nonpolar solvents, probably due to high covalent cross-link density in higher ranked coals.

The concentration of spin probe I as a function of swelling solvent and carbon content of the APCS coals, at 298 K, is shown in Figure 2. Carbon content was used as an indicator of rank throughout this study. Of the three solvents used in this study, pyridine was the most polar, toluene the least. At room temperature, the spin concentration of spherical TEMPOL in the swelled coals decreased with rank for coals swelled with either toluene or nitrobenzene. For coals below about 85 % carbon content (dmmf) swelled in nitrobenzene contained a higher spin probe concentration than coals swelled in toluene. For coals with greater than 85 % carbon content (dmmf), there was no significant difference in spin probe concentration regardless of rank or swelling solvent. Coals swelled with pyridine did not retain TEMPOL to any significant degree.

Coal has been shown by SANS (20, 21) experiments to contain spherically shaped pores. Coal swelled in a mild swelling solvent like toluene at room temperature still retains a significant quantity of spherical pores. At room temperature, nitrobenzene, a moderately polar swelling solvent, caused an increase in the number of the spherically shaped pores and a subsequent increase in the number of trapped smaller spherical shaped probe I. However, when coal underwent more severe swelling, such as in pyridine, pores lost their sphericity and became enlarged and elongated or cylindrical (20, 21) in shape. As a result, the spherical TEMPOL molecules are not retained when the coals were washed with cyclohexane.

The severity of swelling is not only affected by solvent polarity, but also by temperature. An increase in swelling temperature from 288 K to 333 K, while small, had a significant effect on the pore

structure of coal. In Figure 3, the concentration of spin probe I as a function of swelling solvent and carbon content of the APCS coals at 333 K is shown. Again, for higher ranked coals (above 85 % carbon content), spin probe concentration did not vary significantly regardless of rank or swelling solvent. For lower ranked coals, toluene-swelled coals retained a significant number of spherically shaped pores, while coals swelled in pyridine did not. Interestingly, at 333 K, coals swelled in nitrobenzene no longer contain significant quantities of spherically shaped pores.

The swelling process using nitrobenzene and pyridine result in a break-up of the hydrogen bonding system, causing an elongation of the pore structure. For nitrobenzene this was most noticeable using spin probe XIII at 298 K and at 333 K. Spin probe XIII is long and cylindrical in shape. When the APCS coals were swelled in nitrobenzene at room temperature (Figure 4), a significant number of cylindrical pores were present, as were numerous spherical pores. When the swelling temperature was increased to 333 K, the spherical pores all but disappeared, and the number of cylindrical pores increased significantly (Figure 5).

Lack of space prevents a discussion of the effect of temperature on the optimal elongation length deduced using several different spin probes for each solvent as a function of coal rank. However using spin probe V shows that almost no detectable spin probes of the size for which probe V would be trapped occurred at room temperature for toluene, or nitrobenzene or pyridine. However at 333 K, pyridine exhibited significant and measurable concentration of elongated pores similar to that of probe V while none were observed for toluene or nitrobenzene solvents. The variation in concentration with coal rank was similar to that exhibited by spin probe XIII in nitrobenzene.

The effect of temperature on the spin probe concentration of spin probe I depicted in Figures 2-5 appears to suggest the following. For coals swelled in toluene, the number of spherically shaped pores increased with temperature. Higher temperatures increased the ability of toluene to swell coal, but not enough to cause pore elongation. For nitrobenzene, spin probe concentration of I decreases with temperature. Like toluene, higher temperatures increase the ability of nitrobenzene to swell coal. At room temperature, nitrobenzene swelled the APCS coals enough to open up spherical pores. At 333 K, conditions were severe enough for nitrobenzene to cause pore elongation. Pyridine was such a severe swelling solvent for coal that even at room temperature pore elongation occurred.

Extensive Electron Nuclear Double Resonance (ENDOR) studies have shown that little chemical interaction occurs between the coal structure and the spin probes. Lack of space prevents a full discussion of the probe location in the pores of the coal.

CONCLUSION

The use of nitroxide spin probes with swelling solvents is a simple way in which to gain an understanding of the pore structure of coals and how it changes in the presence of swelling solvents. Coal contains significant quantities of spherically shaped pores increasing with decreasing rank. If coal is mildly swelled with nitrobenzene, the number of spherically shaped pores increases. As solvent polarity increases, or as swelling temperature increases such as with pyridine, swelling conditions become more severe. As swelling severity increases, pores become elongated as evidenced by a decrease in the number of spherically shaped pores and a similar increase in the number of elongated pores. Finally, regardless of the severity of swelling conditions within the range studied, the pore structure of high rank coals changes very little.

ACKNOWLEDGEMENT

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Table 1. Major element composition of Argonne Premium Coal Samples, dmmf basis.

Coal	% C	% H	% N	% S	% O
Upper Freeport	88.08	4.84	1.60	0.76	4.72
Wyodak-Anderson	76.04	5.42	1.13	0.48	16.90
Illinois No.6	80.73	5.20	1.43	2.47	10.11
Pittsburgh No. 8	84.95	5.43	1.68	0.91	6.90
Pocahontas	91.81	4.48	1.34	0.51	1.66
Blind Canyon	81.32	6.81	1.59	0.37	10.88
Lewis-Stockton	85.47	5.44	1.61	0.67	6.68
Beulah-Zap	74.05	4.90	1.17	0.71	19.13

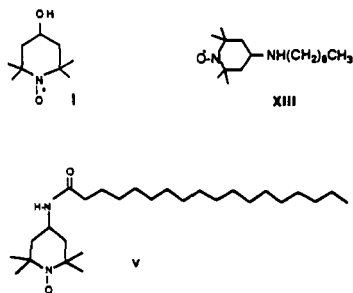


Figure 1. Molecular structure of spin probes I, V and XIII.

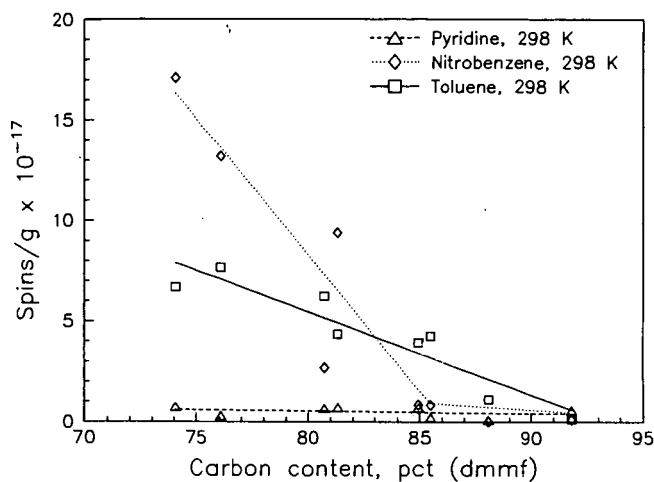


Figure 2. Spin probe concentration of spin probe I (spins/g $\times 10^{17}$) vs. carbon content (pct (%), dmmf basis) for APCS coals swelled 298 K in toluene (\square), nitrobenzene (\diamond), and pyridine (Δ).

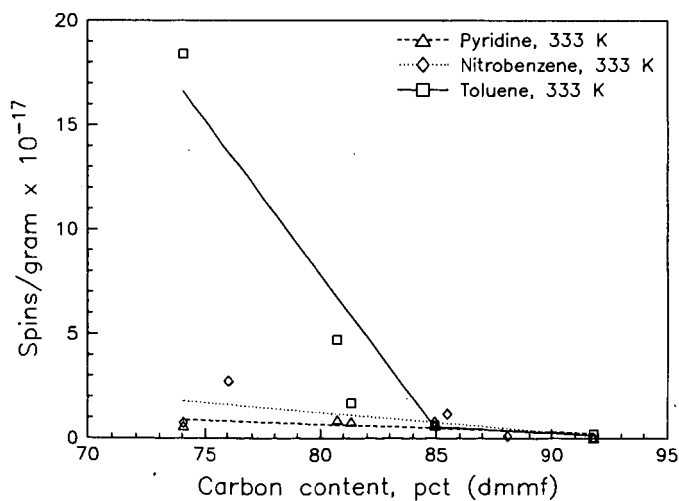


Figure 3. Spin probe concentration of spin probe I (spins/g $\times 10^{17}$) vs. carbon content (pct (%), dmmf basis) for APCS coals swelled 333 K in toluene (\square), nitrobenzene (\diamond), and pyridine (Δ).

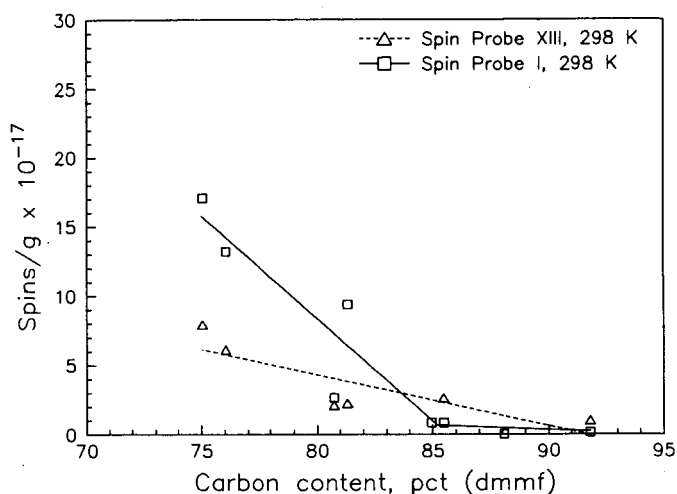


Figure 4. Spin probe concentration of spin probe I (\square) and XIII (Δ) in nitrobenzene at 298 K vs. carbon content (pct (%), dmmf basis) for APCS coals.

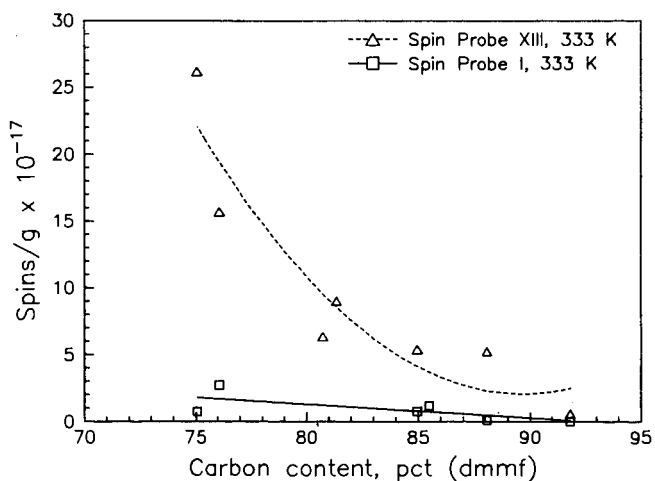


Figure 5. Spin probe concentration of spin probe I (\square) and XIII (Δ) in nitrobenzene at 333 K vs. carbon content (pct (%), dmmf basis) for APCS coals.

SWELLING PRETREATMENT OF COALS FOR IMPROVED LIQUEFACTION

Levent Artok, Harold H. Schobert, Gareth D. Mitchell* and Alan Davis*
Fuel Science Program and Energy and Fuels Research Center*
The Pennsylvania State University
University Park, Pa 16802

Keywords: Molybdenum sulfide catalyst, catalyst dispersion, coal swelling, low severity liquefaction.

INTRODUCTION

The organic fraction of coal can be considered to be a large three-dimensional crosslinked macromolecular network of aromatic clusters connected by etheric and aliphatic bridges with the lower molecular weight species trapped in both open and closed pores or weakly bound to the network¹⁻². The coal network can be swollen using appropriate solvents, leading to the expansion of the pores in it. The extent of swelling is rank-dependent. The swelling of coal facilitates impregnation of catalysts and diffusion of reagents towards the reactive sites of coal. Therefore, it can be presumed that the swelling as a pretreatment operation may increase conversion and quality of yield obtained from liquefaction.

Rincon and Cruz³ found that the conversion of a Colombian coal increased when it is swollen with tetrahydrofuran (THF). Joseph⁴ determined a direct correlation between the extent of preswelling and the conversion of coal under liquefaction conditions.

In our work, the effect of swelling on liquefaction has been investigated with and without catalyst at a pretreatment temperature of 275°C using $(\text{NH}_4)_2\text{MoS}_4$ [ATTM] as a catalyst precursor. In addition, the activities of ATTM and MoS_3 catalyst precursors were compared for unswollen coals at 275°C.

EXPERIMENTAL

Coal preparation

Samples of Blind Canyon high volatile bituminous coal (PSOC-1503 and DECS-6) and Big Brown Texas lignite (PSOC-1444 and DECS-1) collected at different dates were used for this work. The origin and analyses of the coals are given in Table 1. The coals were ground without drying to minus 60 mesh and stored under a nitrogen atmosphere.

Catalyst preparation

ATTM was synthesized in our laboratory following the procedure of Naumann⁵. Molybdenum trisulfide was prepared by acidifying an aqueous solution of ATTM with formic acid, followed by washing the precipitate and drying at 110°C in a vacuum oven.

Sulfur analysis of the molybdenum compounds was performed by the Penn State Materials Characterization Laboratory using a Leco iodimetric titration sulfur analyzer and in the Penn State Combustion Laboratory using a Leco Model SC-132 sulfur analyzer. Carbon, hydrogen, nitrogen analyses were performed using a Leco Model CHN-600 elemental analyzer. Molybdenum analysis and water analysis by the Karl Fisher method were performed by Galbraith Laboratories, Inc. Elemental values and water content of samples are given in Table 2.

Measurement of swelling ratio

One gram of air-dried coal (PSOC-1444 and PSOC-1503) was placed in a 15 ml conical graduated screw-top centrifuge tube and centrifuged at 2900 rpm for 10 minutes and the height of the coal in the tube was recorded in ml/g. Twelve ml of solvent was added to the coal in two increments. The first 6 ml was combined with the coal and the mixture was stirred carefully until all the coal particles were wetted, then

the remaining solvent was added and the tube was sealed with a cap. After a period of time (6-30h) the tube was centrifuged again at 2900 rpm for 10 min and the height was recorded. The volumetric swelling ratio is defined as $Q = h_2/h_1$, where h_1 = height of unswollen coal and h_2 = height of swollen coal.

The swelling procedure of coals

The coal samples (DECS-1 and DECS-6) were swollen using methanol, pyridine, THF and 10% tetrabutylammonium hydroxide (TBAH) solution of 1:1 (v/v) ratio water:methanol mixture. The coal samples, which were predried at 110°C in vacuum, were mixed with the swelling reagent to give approximately a solvent-to-coal ratio of 3:1 (v/w) and were stirred for 6 hours under nitrogen. The solvent was removed and dried at 50°C in vacuum. In the case of pyridine, the sample was dried at 100°C in vacuum in an attempt to remove pyridine completely. In the case of TBAH, a TBAH solution was added to undried coal and only methanol and water of the mixture were removed, so that TBAH was retained in the swollen coal matrix.

Impregnation of swollen and unswollen coals with catalyst precursors

The catalyst precursor was loaded onto the coal in an amount based on 1% molybdenum (as the metal, not the molybdenum compound) on a dry ash free (daf) basis regardless of whether the coal had been swollen or not. Unswollen coals were impregnated with a water solution of ATTM or suspension of molybdenum trisulfide. The procedure consisted of dissolving or suspending the molybdenum salts in enough distilled water to give an approximate water-to-coal ratio of 1:1 (v/w). Then this solution or suspension was added to coal and stirred for 30 min before solvent removal. Excess water was removed from the mixture at room temperature in vacuum. The mixture was continuously being stirred during this procedure. Subsequently, the mixture was quenched in a dry ice-acetone bath until it became frozen and was then freeze dried, followed by vacuum drying at room temperature.

In the case of swollen coal, the swelling reagent (except TBAH) was removed in vacuum at room temperature. While the coal was still wet with swelling reagent, enough ATTM solution (which had been prepared by dissolving ATTM in 1:1 (v/v) ratio methanol:water mixture) to give solution-to-coal ratio of 1:1 (v/w) was added to coal and stirred for 30 min. In the case of TBAH, ATTM was dissolved in a 10% TBAH solution of 1:1 ratio (v/v) water:methanol mixture, then this solution was added to undried coal and stirred for 6 hours in order to give enough time for swelling of coal under nitrogen. After stirring, excess solvent was removed at room temperature in vacuum while it was continuously being stirred, and finally vacuum drying was applied at 50°C for the coals swollen with methanol, THF or TBAH, or at 100°C for pyridine-swollen coal. TBAH was allowed to remain in the coal.

The TBAH content of samples, whether catalyst-impregnated or not, was calculated from the increase of the nitrogen content of the coals, measured with a Leco Model CHN-600 analyzer.

Liquefaction reaction and yield fractionation

The liquefaction reactions were performed in horizontal microautoclave reactors (tubing bomb) of nominal 25 ml capacity. The procedure was the same for both preswollen and unswollen coals and also the same whether they had been impregnated with a catalyst or not.

Five grams of each prepared coal sample and five grams of phenanthrene were placed in the tubing bomb. After mixing the contents with a spatula, the reactor was sealed, pressurized to 1000 psi with nitrogen and checked for leaks. The depressurized tubing bomb was purged with hydrogen twice, pressurizing and depressurizing to 1000 psi. Subsequently, the tubing bombs, pressurized to 1000 psi with hydrogen, were attached to a vertically oscillating system fluidized sand bath which was heated to 283 °C. Immediately after the tubing bombs were placed in the sand bath, the thermostat was reset to 275°C, which was the desired pretreatment temperature. The tubing bombs attained a temperature of 275 °C in about 30 seconds. All the pretreatment experiments were done in duplicate 30 min. reaction times. During this period, the tubing bombs were oscillated through an amplitude of 2 cm at 350 cycles/min.

At the end of the reaction, the reactors were rapidly quenched to room temperature by immersion in cold water. After venting the gas, the contents of each bomb were quantitatively washed into a tared ceramic thimble using toluene and Soxhlet extracted with toluene under nitrogen until the solvent appeared colorless. The toluene extract was concentrated to 10-20 ml by rotary evaporation. The extract was diluted with 400 ml of hexane. The mixture was stirred for 1 h and asphaltenes were allowed to settle overnight and separated with 0.45 micron filter. The filtrate containing hexane-solubles was evaporated by rotary evaporation to remove the hexane. Toluene insolubles were Soxhlet-extracted with THF to separate preasphaltenes and the solid residue under nitrogen atmosphere. THF was removed from the extract by rotary evaporation. Preasphaltenes, asphaltenes and residue were dried overnight in vacuum at 110°C. The conversion was calculated by subtracting residue weight (catalyst corrected) from the weight of coal and dividing by the daf weight of the coal. It was assumed that the catalyst precursor transformed to the same product as ATTM processed without coal in hydrogen at 275°C (Table 2).

RESULTS AND DISCUSSION

Swelling of coals

Solvent swelling ratios with contact time for four different solvents are given in Tables 3 and 4 for Texas lignite (PSOC-1444) and the Blind Canyon hvCb (PSOC-1503), respectively. The maximum level of swelling was attained within 6 h; additional solvent-coal contact in excess of 26 h did not produce a significant increase in swelling ratio. The level of swelling experienced for each coal was slightly different with respect to the individual solvents. For the Texas lignite, swelling increased in order of methanol < THF < pyridine < 10% TBAH; for the Blind Canyon hvCb coal the order was 10% TBAH < methanol < THF < pyridine. Note that the level of the swelling for the different solvents appears to be rank-dependent. Lignites are more crosslinked than bituminous coals. Therefore, lignites give less swelling and extractability for methanol, THF and pyridine than bituminous coals. Lignites have more acidic functional groups (phenolic hydroxyl and carboxylic groups) than bituminous coals; therefore, swelling of lignite increases with increasing basicity of solvents. TBAH is quite basic and has been shown to react strongly with the types of oxygen functionalities in most lower rank coals⁶. Joseph⁴ determined for the Illinois #6 bituminous coal that the highest swelling was obtained with 15% TBAH compared with those of THF and methanol. This can be explained, in part by the much higher oxygen functionality of the Illinois #6 coal than that of the Blind Canyon coal and the tendency for TBAH to react with these functional groups⁶.

Comparison of MoS₃ and ATTM catalysts for pretreatment

Table 5 shows the conversion data of thermal (non catalytic) and catalyst-impregnated coals. The conversions of coals with both catalysts are greater than those obtained without catalyst. ATTM effectively enhances preasphaltenes and asphaltenes formation for both coals and also improves oil yield for Blind Canyon coal (DECS-6), but not for of the Texas lignite (DECS-1). MoS₃ improved only preasphaltene yield for the Texas lignite; it has not affected formation of asphaltenes and of oil. For the Blind Canyon coal with MoS₃, preasphaltenes were 8% greater than those obtained without catalyst. This yield was even higher than obtained with ATTM, and greater conversion was obtained than with ATTM. However, oil yield was not improved with MoS₃. The conversion of Illinois #6 coal with MoS₃ was found to be comparable to that obtained with ATTM⁷. ATTM was reacted at 275°C under hydrogen atmosphere (1000 psi cold) without coal in order to determine the fate of ATTM at the preliquefaction conditions used in this work. Elemental analysis of the product shows 3.26% of nitrogen (Table 2). The different activities of these catalysts with both coals, may be due to dependence of dispersion on the type of coal and on the destructive effect of ammonia, released from decomposition of ATTM, on catalytic activity of molybdenum sulfide catalyst.

The effect of preswelling on liquefaction

The conversion results of solvent swollen coals without catalyst impregnation are given in Tables 6 and 7. The treatment with methanol enhanced oil formation, decreased preasphaltenes and asphaltenes for the Texas lignite (DECS-1); enhanced oil and preasphaltenes, decreased asphaltenes for the Blind Canyon coal (DECS-6). THF is the least effective swelling reagent in terms of liquefaction of the Texas lignite. It

provided great conversion with its high swelling ability for the Blind Canyon coal ($Q=1.9$). THF pretreatment increased total conversion of the Blind Canyon coal from 17.7% to 22.1% and oil formation from 4.9% to 9.2%, but its effect on formation of preasphaltenes is not significant and did not influence formation of asphaltenes. The pyridine pretreatment provided greater total conversion and oil formation for the Texas lignite than those obtained from methanol- and THF- treated coals. However, this treatment diminished formation of preasphaltenes for this coal. The pyridine treatment for Blind Canyon coal, surprisingly, decreased total conversion from 17.7% to 16.0%, formation of preasphaltenes from 10.7% to 6.4%, asphaltenes from 2.1% to 1.3%, but increased formation of oil from 4.9% to 9.2%. TBAH treatment provided the highest conversion for the both coals relative to the other solvents, even though 10% TBAH solution in 1:1 water:methanol mixture swelled the Blind Canyon coal least. There might be two reasons for the high conversion with TBAH addition onto coals. The first is the swelling effect. The evaporation of methanol and water from mixture increases the concentration of TBAH. The TBAH thus, concentrated by evaporation can increase the level of swelling of the coal, even for Blind Canyon. Second, in a reaction of 40% TBAH in a tubing bomb at the same reaction conditions as pretreatment experiments (but without coal), butane and butene were observed in the gaseous products. It can be expected that TBAH likely transformed to amine compounds. Therefore, TBAH is going to act as a solvent precursor. It has been found that amines are very good promoters for coal liquefaction⁸⁻⁹⁻¹⁰. The nitrogen contents of residue, preasphaltenes and asphaltenes were found to be higher for TBAH-swollen coal than those of unswollen coal. This increase can be attributed to incorporation of amines. Therefore, assuming that TBAH transformed to tributylamine, the amount of tributylamine incorporated in residue, asphaltenes and preasphaltenes can be determined from their difference of nitrogen content and those of the respective products from unswollen coal (Table 10). Incorporation of tributylamine in the residue of the Texas lignite is greater than in Blind Canyon, and addition of catalyst increased this incorporation. Addition of TBAH provided the highest increase in yields of preasphaltenes, asphaltenes and oil for the Texas lignite compared to those of coals swollen with other solvents. For the Blind Canyon coal, TBAH addition provided the greatest conversion, yields of preasphaltenes and asphaltenes, but a lower yield of oil relative to those for coals swollen with the other solvents. For the Texas lignite, conversion without catalyst increased in the order of none < THF < methanol < pyridine < TBAH. For the Blind Canyon coal conversion without catalyst increased in the order of pyridine < none < methanol < THF < TBAH. The extractive ability of a particular solvent is related to the swelling effect of that solvent for a particular coal. A good extractive solvent can disrupt weak bonds in the coal network or in material trapped in the coal structure. Therefore, the molecules released by this disruption and the weakened structure can be liquefied at less severe conditions.

Comparative conversion data of ATTM-impregnated swollen Texas lignite and Blind Canyon are given in Tables 8 and 9. For the Texas lignite with ATTM catalyst the effect of swelling on formation of preasphaltenes and asphaltenes decreases, except for TBAH. The greatest conversions and formation of all types of products were obtained with TBAH addition. If these data were compared with those obtained without catalyst, it can be seen that addition of ATTM increased total conversion and formation of preasphaltenes and asphaltenes, but did not change the amount of oil. The order of conversion can be given as none < THF, methanol < pyridine < TBAH for the Texas lignite. For the Blind Canyon coal methanol treatment decreased yield of asphaltenes, but did not affect conversion and yields of other products. THF treatment decreased formation of preasphaltenes and asphaltenes, while it provided the greatest yield of oil relative to other solvents. However, THF treatment did not affect total conversion. Pyridine treatment decreased formation of preasphaltenes and asphaltenes while increasing total conversion and formation of oils. TBAH addition seemed to decrease the activity of the molybdenum sulfide catalyst, because the conversion of TBAH-treated coal was less than unswollen coal. The addition of ATTM to swollen coals increased significantly total conversion and formation of yields for the Blind Canyon coal except TBAH added coal. The order of conversion is noticed as TBAH < none, methanol, THF < pyridine

CONCLUSIONS

Without swelling pretreatment, impregnation of both coals increased conversion at 275°C. The increased conversion was mainly a result of an increased yield of preasphaltenes. In the absence of catalyst, swelling the Texas lignite before liquefaction improves conversion, with the increase mainly a result of additional (oil+gas) yield. The relative effectiveness of various solvents for improving conversion is in the same general order as their effectiveness at swelling the coal. Preswelling with methanol or

pyridine has little effect on liquefaction of the Blind Canyon coal, but both THF and TBAH provide increased conversion, as a result of improved preasphaltene yields. With this coal, the effectiveness of solvents at improving liquefaction is not in the same order as their ability to swell the coal. The combined effect of catalyst addition and swelling is to enhance conversion of the lignite, with a doubling of conversion obtained by impregnation with ATTM and swelling by TBAH. The yields of all products are enhanced by this pretreatment. In contrast, little improvement in total conversion of the Blind Canyon coal is obtained by combining ATTM impregnation and solvent swelling, but changes in the relative proportions of the products can be obtained.

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Table 1. Characteristics of coals.

<u>Sample No.</u>	<u>PSOC-1444</u>	<u>PSOC-1503</u>	<u>DECS-1</u>	<u>DECS-6</u>
Seam	Unnamed	Blind Canyon	Bottom	Blind Canyon
County	Freestone	Emery	Freestone	Emery
State	Texas	Utah	Texas	Utah
Province	Gulf	Rocky Mt.	Gulf	Rocky Mt.
Sampling Date	3/30/85	10/01/85	12/11/89	6/07/90
ASTM rank class	Lignite	hVC b	Sub	hVB b
Moisture Content % wt	31.91	10.35	30.00	4.73
Min. Matter % wt (dry)	19.02	4.36	17.97	6.67
<u>Elem. Comp. (% dmmf)</u>				
C	76.21	80.80	76.13	81.72
H	4.71	6.12	5.54	6.22
N	1.42	1.55	1.5	1.56
S (org)	1.36	0.54	1.05	0.40
O (diff)	16.29	10.58	15.78	10.10

Table 2. Elemental analysis of ATTm, MoS₃ and the product obtained from microautoclave reaction of ATTm at 1000 psi (cold) hydrogen gas at a temperature of 275 °C.

Catalyst	%N	%H	%Mo	%S	%H ₂ O	nS:nMo
ATTm	10.81	3.10	37.01	49.15	ND	3.98
MoS ₃	ND	ND	44.45	50.50	1.39	3.41
HATTm*	3.26	1.40	49.74	39.40	6.36	2.38

ND = Not determined.

* = Hydrogenated ATTm

Table 3. Change in solvent swelling ratio (Q) with time for the Texas Lignite (PSOC-1444).

Methanol		THF		Pyridine		TBAH	
Time (h)	Q	Time (h)	Q	Time (h)	Q	Time (h)	Q
5.0	1.1	6.0	1.2	6.5	1.6	6.0	2.6
11.5	1.1	16.5	1.2	21.5	1.6	14.5	2.6
23.0	1.1	22.0	1.3	42.0	1.6	24.5	2.7
27.5	1.1	28.0	1.3				

Table 4. Change in solvent swelling ratio (Q) with time for the Blind Canyon hvCb coal (PSOC-1503).

Time (h)	Methanol Q	THF Q	Pyridine Q	TBAH (10%) Q
6.0	1.2	1.9	2.4	1.2
10.0	1.3	1.8	2.3	1.2
20.0	1.3	1.8	2.2	1.2
26.0	1.3	1.8	2.3	1.2

Table 5. The activity of ATTm and MoS₃ on liquefaction of (Texas lignite) DECS-1 and (Blind Canyon hvB) DECS-6 coals at 275°C.

Coal	Catalyst	Conversion % (daf)			
		Total	Preasph.	Asphal.	Oil + Gas
DECS-1	None	6.6	2.8	2.2	1.6
"	ATTm	9.0	3.9	3.6	1.5
"	MoS ₃	7.2	3.9	1.7	1.6
DECS-6	None	17.7	10.7	2.1	4.9
"	ATTm	25.0	15.1	3.0	6.9
"	MoS ₃	26.9	19.0	3.3	4.6

Table 6. Effect of preswelling treatment on liquefaction of Texas lignite (DECS-1) at 275°C.

Sol. Treat.	Conversion %(daf)			
	Total	Preasphalt.	Asphal.	Oil +Gas
None	6.6	2.8	2.2	1.6
Methanol	8.4	2.2	1.8	4.4
THF	7.4	2.9	0.9	3.6
Pyridine	10.0	1.7	2.0	6.4
TBAH	17.5	5.2	3.9	8.4

Table 7. Effect of preswelling treatment on liquefaction of Blind Canyon hvB (DECS-1) at 275°C.

Sol. Treat.	Conversion %(daf)			
	Total	Preasphalt.	Asphal.	Oil +Gas
None	17.7	10.7	2.1	4.9
Methanol	19.8	12.2	1.6	6.0
THF	22.1	11.1	2.2	9.2
Pyridine	16.0	6.4	1.3	8.2
TBAH	24.0	15.1	3.6	5.3

Table 8. Effect of preswelling on liquefaction of Texas Lignite with ATTM catalyst at 275°C.

Sol. Treat.	Conversion %(daf)			
	Total	Preasphalt.	Asphal.	Oil+Gas
None	9.0	3.9	3.6	1.5
Methanol	9.5	2.8	2.2	4.5
THF	9.3	3.1	2.8	3.4
Pyridine	11.8	2.9	2.4	6.5
TBAH	18.7	6.2	4.6	7.9

Table 9. Effect of preswelling on liquefaction of Blind Canyon hvB with ATTM at 275°C.

Sol. Treat.	Conversion %(daf)			
	Total	Preasphalt.	Asphal.	Oil + Gas
None	25.0	15.1	3.0	6.9
Methanol	24.7	15.4	2.4	6.9
THF	25.1	12.4	2.4	10.3
Pyridine	26.7	14.6	2.6	9.5
TBAH	23.7	13.5	3.9	6.3

Table 10. The percentage of tributyl amine incorporated to residue, preasphaltenes and asphaltenes of TBAH treated Texas lignite (DECS-1) and Blind Canyon hvB (DECS-6) after hydrogenation with or without ATTM.

Coal	ATTM	Incorporation of TBAH %(dry)		
		Residue	Preashalt.	Asphal.
DECS-1	No	3.2	4.7	5.0
DECS-1	Yes	4.3	3.8	5.5
DECS-6	No	1.7	2.1	8.6
DECS-6	Yes	4.3	3.8	5.5

Morphology and Liquefaction Characteristics of
Pyridine-Extracted Illinois No. 6 Coal

R. P. Warzinski and G.D. Holder¹

U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA 15236

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Introduction

The primary goal of preconversion processing of coal prior to direct liquefaction is to alter the coal in some fashion so that hydrogenation reactions are favored and detrimental, regressive reactions are limited during the subsequent liquefaction. For example, catalytic hydrogenation at 300-350°C has been shown to favorably influence the yield and composition of products produced during catalytic liquefaction at 400°C (1). Other work has indicated that the glassy nature of coal itself may promote retrogressive pathways that would not exist if the coal structure had more mobility and flexibility (2). Altering the structure of coal by solvent swelling has also been shown to result in improved conversion in noncatalytic, donor-solvent liquefaction (3). As others have postulated, this may be due to the improved penetration and diffusion of reagents in the distorted structure of the swollen coal (4,5) and/or to the possible reduction in the glass transition temperature (used loosely for coal) of the swollen product (6,7).

When coal is swollen and extracted with pyridine, extensive morphological changes are known to occur (4,8,9). The magnitude of the changes in the surface area and porosity of the pyridine-insoluble product may be influenced by the manner in which the residual pyridine is removed. Work with highly porous, silica aerogels indicates that processes involving evaporative removal of a swelling solvent may result in partial collapse of the expanded structure owing to surface-tension effects on the walls of the pores generated by the leaving solvent (10). Maximum porosity is achieved in these systems if non-evaporative methods of solvent removal are used. One such method that avoids the formation of a liquid-vapor interface in the solvent removal process is the dissolution and removal of the swelling solvent by a supercritical fluid (SCF).

In the work reported here, three Illinois No. 6 coal samples were swollen and extracted with pyridine and then subjected to both vacuum drying and SCF extraction with CO₂ to remove the residual pyridine. Differences in morphological features and liquefaction behavior were observed depending on which technique was used. Tests were also performed to compare the liquefaction behavior of the pyridine-soluble fraction with the pyridine-insoluble portion of the coal.

Experimental

The work reported here was performed on three samples of minus 100-mesh Illinois No. 6 coal. Two were from the Burning Star mine and were prepared at the Pittsburgh Energy Technology Center. The third was from

¹ University of Pittsburgh, Pittsburgh, PA 15216

the Argonne Premium Coal Sample program. Elemental analyses of these coals are contained in Table 1.

Pyridine swelling and initial extraction were performed in an Erlenmeyer flask. The coal was added to an excess (approximately 6.5:1 on a weight basis) of reagent-grade pyridine and stirred for approximately two days with a magnetic stirrer. The slurry was then transferred to a cellulose Soxhlet thimble and exhaustively extracted with fresh pyridine until the extract was nearly colorless (pale yellow). The thimble was then removed and the excess pyridine allowed to drain away. The pyridine-insoluble product (PIP) recovered from the Soxhlet thimble contained about 2.5 times its original weight in pyridine. The pyridine-soluble product (PSP) was recovered by rotary evaporation.

Vacuum-dried samples of the PIP were prepared by placing a portion of the material recovered from the Soxhlet thimble in an oven at 110°C to 115°C under full vacuum supplied by a mechanical vacuum pump. The sample was dried in this fashion until the weight loss after a 1-hour interval was less than 0.5%.

Another portion of the PIP from the Soxhlet thimble was extracted with supercritical CO₂ (T_c - 31°C, P_c - 1056 psig) to remove the excess pyridine. The SCF extractions were performed in either a small (1.0 cm i.d. by 25.0 cm long) or large (2.2 cm i.d. by 50.0 cm long) empty HPLC column. The column was wrapped with heating tape, insulated, and connected to a high-pressure ISCO syringe pump filled with liquid CO₂ (375 cm³ capacity). A back-pressure regulator was used after the column to control the pressure during the extraction. Thermocouples inserted into tee fittings at each end of the column were used to monitor the extraction temperature. With the larger column, another thermocouple was clamped to the surface at its midpoint. Auto-transformers were used to control the heating tapes on the column and on the inlet and exit lines. During the extraction, the column temperature was maintained at 40°C to 45°C and the back-pressure regulator was set at 2000 psig.

When using the small column approximately 12 g of the PIP was extracted. After heating the column, the extraction involved first pumping about 135 ml of CO₂ (as measured on the syringe pump scale) at 10 ml/hour and then 270 ml at 40 ml/hour. The unit was then slowly depressurized through a needle valve while maintaining the temperature at 40°C. The column was then removed and transferred to a nitrogen-filled glove box for sample recovery.

When using the large column, approximately 100 g of the PIP was extracted. The procedure was similar to that for the small column except that more CO₂ was used and at faster flow rates (525 ml at 40 ml/hour then 560 ml at 200 ml/hour). However, on a g-CO₂/g-coal basis, the amount of CO₂ used was less for the larger column, 11 g-CO₂/g-coal as compared to 34 g-CO₂/g-coal for the smaller column.

Surface area measurements, helium densities, and mercury densities were performed at the Center for Micro-Engineered Ceramics at the University of New Mexico by Dr. Douglas Smith. The surface area measurements included a five-point nitrogen analysis at 77 K and a four-point CO₂ analysis at 298 K. The nitrogen measurement provides an estimation of the surface area present in pores with diameters greater than 0.4 nm; whereas, the carbon dioxide measurement is believed to represent the total surface area of coal, including occluded pores (8,9).

Liquefaction tests were performed in a 38 cm³ (2.54-cm o.d., 12.7-cm long) stainless-steel microautoclave, which was horizontally positioned in a fluidized sandbath and agitated at 360 cycles-per-minute by a Burrell wrist-action shaker. The microautoclave was rapidly heated to reaction temperature by immersion in the hot sand bath and quenched after reaction in water. The internal temperature and pressure were continuously monitored. The microautoclave was charged with approximately 3 g of coal or extraction product, 6 g of tetralin (if used), 1600 to 5000 ppm (based on metal) of a molybdenum-containing catalyst precursor (if used), 0.3 g of carbon disulfide, and 1000 psig hydrogen. When using a catalyst precursor, it was dissolved in only enough solvent to form a wet paste with the sample. The solvent was then removed, usually under vacuum at 60°C, before the liquefaction test. Liquefaction tests were carried out at 425°C for either 20 or 60 minutes. Liquefaction conversions were measured by sequential extraction with either of two sets of solvents -- methylene chloride/n-heptane or tetrahydrofuran/cyclohexane -- using pressure filtration to separate the soluble products from the residues. Conversions were determined from the insoluble residues and are expressed on a dry, ash-free basis.

Results and Discussion

Sample 1 from the Burning Star mine was the first sample swollen and extracted in pyridine. Based on the as-received coal and the actual amount of solvent-free PIP recovered, 15% of this coal sample was extracted by pyridine. One portion of the PIP from the Soxhlet thimble was vacuum dried and another portion was extracted with supercritical CO₂ using the small column.

As previously mentioned, the objective of performing the SCF extraction was to remove the pyridine by a non-evaporative process that would avoid the formation of a vapor/liquid interface. A model based on the Peng-Robinson equation-of-state was used to estimate the vapor/liquid phase behavior for the CO₂/pyridine system (11). A binary interaction parameter of 0.080 was used in this calculation. Using this model, the mixture critical point at 40°C was estimated to be near 1160 psig. The operational conditions used, 2000 psig at 40°C, are well above this point. At these conditions, the CO₂ should initially dissolve in and expand the pyridine present in the sample, moving the interface out of the coal pores and quickly causing it to disappear without evaporation. The pyridine concentration in the pores would then be reduced by the continued addition of supercritical CO₂ until all of the physically entrapped pyridine was removed. As opposed to vacuum-drying, no surface-tension effects would be exerted on the walls of the pores by the leaving solvent. In fact, the SCF expansion of the pyridine phase may have the opposite effect in exerting a positive force, which would tend to maintain the porosity of the sample.

Both vacuum drying and SCF extraction should remove all of the physically entrapped, but not chemically associated, pyridine from the PIP. The elemental analyses in Table 1 show that the nitrogen contents of the vacuum-dried and SCF-extracted PIP are similar. Based upon elemental analyses and material balances, 6% to 10% pyridine is estimated to remain in the PIP after either procedure.

Table 2 contains the surface area and density results for both the vacuum-dried and SCF-extracted samples. Also shown in this table are the results from a CO₂-extraction experiment in which all of the conditions were the same as for the SCF extraction, except that the

temperature was maintained at 25°C. Under these subcritical conditions, the extraction would be performed with liquid CO₂. The results in Table 2 show that the vacuum-dried PIP has less nitrogen surface area and porosity than the starting coal, while the CO₂ surface area remains about the same. On the other hand, the end result after removal of the pyridine by SCF extraction is an increase in both the nitrogen and CO₂ surface areas and in the resulting porosity. Compared to vacuum drying, SCF extraction produces a PIP that has 6.5 times the nitrogen surface area, 1.9 times the CO₂ surface area, and 4.2 times the porosity.

The data in Table 2 also show that liquid-CO₂ extraction results in a product with nitrogen and CO₂ surface areas that are respectively equal to and greater than the untreated coal but less in both cases than the supercritical-CO₂ extracted sample. The porosity, however, appears to be more like the vacuum-dried sample than the one from supercritical-CO₂ extraction. This initial data supports the hypothesis that the SCF extraction not only eliminates surface-tension forces that would tend to collapse the expanded structure of the PIP but generates forces that help to maintain the expanded structure.

To further investigate this phenomenon, the Argonne Premium Coal sample was subjected to the same treatment described above, except the liquid-CO₂ extraction was not performed. The handling of the untreated coal and the Soxhlet extraction were performed under nitrogen to limit the exposure of this coal to air. This coal sample was found to be 33% soluble in pyridine (based on as-received coal and actual weights recovered). This is twice that of the Burning Star sample discussed above. Similar differences in pyridine extractability between premium and non-premium Illinois No. 6 coal samples have been reported (12,13). Surface area and density results for the vacuum-dried and SCF-extracted samples are also contained in Table 2. All of the trends noted previously for the Burning Star sample are observed in the results for the Argonne coal. The changes in the nitrogen surface areas are particularly noteworthy. The porosity achieved with the SCF extraction was nearly the same as for the Burning Star sample.

Analysis of the SCF-extracted PIP from the Burning Star sample over a period of time showed the increases in surface areas and porosity to be a transitory phenomenon. Surface area and porosity determinations made on fresh aliquots taken from the sample over a four-month period are shown in Figure 1. These results show that the nitrogen surface area, the carbon dioxide surface area, and the porosity decrease with time. The last reported nitrogen and porosity values are even less than for the starting coal and approach the values for the vacuum-dried sample, which are represented in Figure 1 by the open symbols.

Microautoclave liquefaction tests were performed on a second sample of the Burning Star coal which was swollen and extracted with pyridine as before. To prepare enough material, the large column was used for the SCF extraction. The pyridine solubility of this second sample was 23%, which is higher than the first sample of this coal but still less than the Argonne sample.

The vacuum-dried and SCF-extracted samples of the PIP from the second sample of Burning Star coal were used in both thermal and catalytic microautoclave liquefaction experiments to determine the effects of the different morphology on conversion. Ammonium heptamolybdate (AHM) was used as the catalyst precursor at about 5000 ppm (based on metal) in the catalytic tests. A summary of these results is contained in Figure 2. The first two pair of tests in this figure were made using tetralin,

both with and without AHM. The conversions to methylene chloride and heptane solubles were slightly higher in both cases for the SCF-extracted PIP than for the vacuum-dried sample, and the greatest difference occurred in the heptane conversion in the catalytic case. The last pair of tests was performed without added solvent, again with 5000 ppm AHM. In this case, the conversions were measured in tetrahydrofuran and cyclohexane. This particular liquefaction and solvent-analysis system accentuates the effects of the pretreatment procedures on the liquefaction conversions.

From these results, the morphological changes associated with the SCF-extracted samples appear to facilitate liquefaction of these samples, especially in the presence of a catalyst. A possible explanation is that the expanded structure caused by this treatment permits the catalyst precursor to better penetrate these samples during the impregnation procedure, resulting in the improved liquefaction conversions. Investigation in this area is continuing to further substantiate and understand these results.

Additional microautoclave tests on both the PSP and the PIP were performed to investigate the fate of these materials during liquefaction. Figure 3 shows the results of subjecting the PSP to liquefaction with and without solvent and catalyst. In these tests, the contact time at 425°C was 60 minutes and the catalyst precursor was ammonium tetrathiomolybdate (ATM) added from water. The first set of bars shows the pre-liquefaction solubilities of the PSP in tetrahydrofuran and cyclohexane. The next test shows that, in the absence of both catalyst and hydrogen-donor solvent, the solubility in tetrahydrofuran drops sharply while the cyclohexane solubility increases. The remaining data in Figure 3 show that the presence of either a hydrogen-donor solvent or catalyst prevents the retrogressive behavior observed in the absence of these compounds. In the data set shown, the presence of a catalyst provides higher conversions than when a hydrogen-donor solvent is used.

The liquefaction results for the SCF-extracted PIP are contained in Figure 4. No hydrogen-donor solvent was used in any of these tests. Adding ATM as previously described improved both the tetrahydrofuran and cyclohexane conversions. A further improvement in the conversions was also noted when the ATM was added from pyridine and then subjected to extraction with supercritical CO₂ to remove the pyridine. In this case, greater penetration of the ATM into the PIP is likely since the pyridine would re-swell the PIP and facilitate transport of the ATM into the particles. Removing the pyridine with supercritical CO₂ would prevent the ATM from being pulled back out of the particles with the leaving solvent, as might be the case if vacuum drying were used. This aspect of the work is under further investigation.

Summary

Our work has shown that a coal sample can be prepared with an expanded structure, that is, one in which the porosity is two to four times as great as the starting coal. This effect is due both to the removal of pyridine-soluble material and to the means of removing the residual pyridine from the insoluble portion. A non-evaporative procedure, such as SCF extraction, leaves the coal structure, at least temporarily, in an expanded state, whereas vacuum drying causes an immediate collapse of the extracted coal. Upon liquefaction, conversions were consistently

higher for samples subjected to SCF extraction compared to vacuum drying. The greatest benefit was observed in the catalytic tests.

Additional liquefaction tests were performed on both the PSP and PIP. The PSP formed a more refractory product when subjected to liquefaction in the absence of both a catalyst and a hydrogen-donor solvent. The presence of either the catalyst or the solvent reduced this retrogressive behavior. The benefit of a catalyst in this situation was marginally greater than the presence of a hydrogen-donor solvent. The importance of a catalyst was also noted in the liquefaction of the PIP. Dispersal of a catalyst precursor in a manner that may be superior to aqueous impregnation resulted in marginal improvements in liquefaction conversions of the PIP.

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Disclaimer

Reference in this report to any specific product, process, or service is to facilitate understanding and does not imply its endorsement or favoring by the United States Department of Energy.

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Table 1. Elemental analyses.

Sample Designation	Moisture	-----moisture free-----					
		Ash	C	H	O	N	S
<u>Burning Star Sample 1</u>							
Untreated Coal	3.5	10.4	69.1	4.7	11.6	1.4	2.9
Pyridine-Insoluble Product							
Vacuum Dried	3.0	12.1	65.7	4.3	12.3	2.1	3.0
SC-CO ₂ Extracted	3.4	11.1	67.0	4.3	11.9	2.3	2.9
Liquid CO ₂ Extracted	4.5	11.4	66.8	4.2	12.9	2.5	3.0
<u>Burning Star Sample 2</u>							
Untreated Coal	2.1	8.6	70.6	5.0	12.0	1.5	2.4
Pyridine-Insoluble Product							
Vacuum Dried	1.0	9.8	69.6	4.7	13.4	2.5	2.5
SC-CO ₂ Extracted	3.2	10.1	70.1	4.9	11.4	2.9	2.4
Pyridine-Soluble Product	10.5	0.6	80.7	6.0	8.8	2.4	1.2
<u>Argonne Premium Sample</u>							
Untreated Coal	4.5	14.8	65.6	4.5	9.4	1.2	4.9
Pyridine-Insoluble Product							
Vacuum Dried	2.4	17.4	63.0	4.1	10.5	2.2	4.8
SC-CO ₂ Extracted	1.6	17.5	63.0	4.2	9.6	1.9	5.0

Table 2. Surface area and density results.

Sample Designation	Surface area, m ² /g		Density, g/cm ³		Porosity*
	N ₂	CO ₂	He	Hg	
<u>Burning Star Sample 1</u>					
Untreated Coal	12.3	93.4	1.47	1.33	0.10
Vacuum Dried	2.6	91.6	1.47	1.40	0.05
SC-CO ₂ Extracted	17.0	170.7	1.46	1.16	0.21
Liquid CO ₂ Extracted	12.6	143.9	1.47	1.38	0.06
<u>Argonne Premium Sample</u>					
Untreated Coal	25.8	76.8	1.46	1.38	0.05
Vacuum Dried	1.7	90.3	1.46	1.42	0.03
SC-CO ₂ Extracted	36.0	111.2	1.47	1.19	0.19

*Porosity = Hg density(1/Hg density - 1/He density)

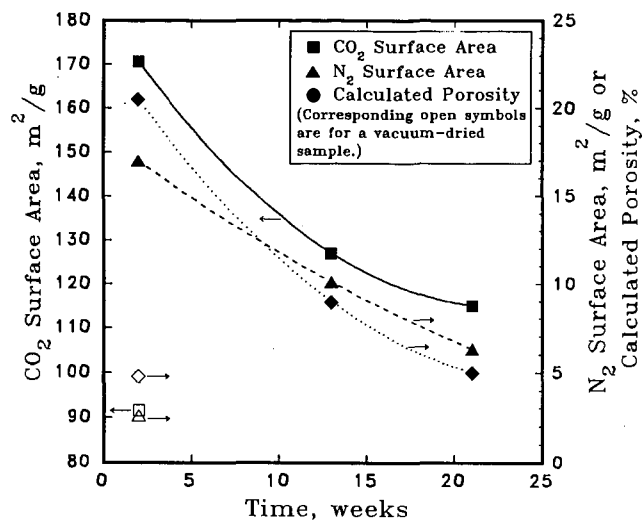


Figure 1. Morphological changes in the SCF-extracted pyridine-insoluble product with time.

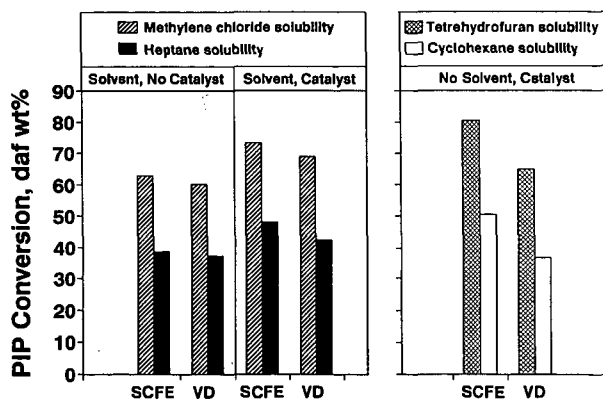


Figure 2. Thermal and catalytic liquefaction of SCF-extracted and vacuum-dried pyridine-insoluble product with and without tetralin and 5000 ppm AHM. SCFE - Supercritical Fluid Extracted. VD - Vacuum Dried. Micro-autoclave tests performed at 425°C, 20 min., 1000 psig hydrogen (cold).

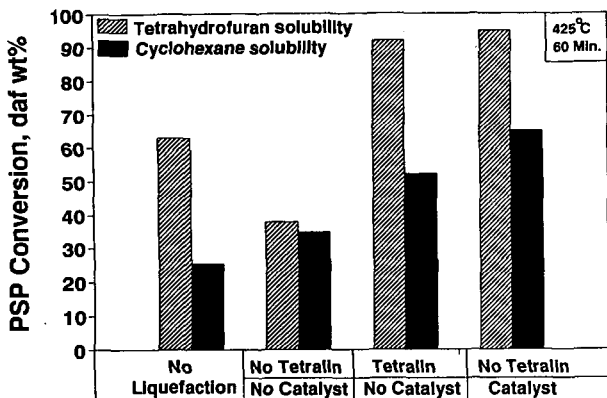


Figure 3. Conversion of pyridine-soluble product in thermal and catalytic liquefaction tests. 1600 ppm Mo added as ATM in the catalytic test. All tests were under 1000 psig hydrogen (cold).

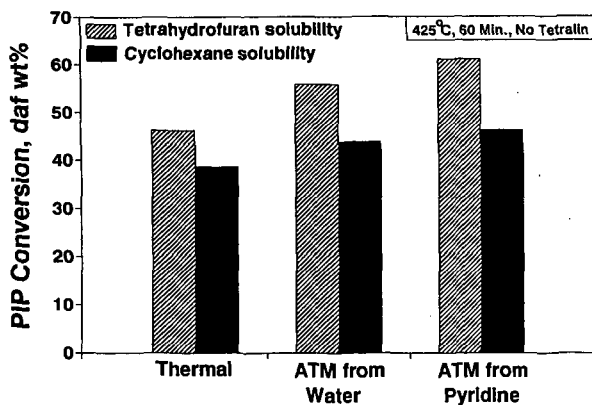


Figure 4. Thermal and catalytic liquefaction of SCF-extracted pyridine-insoluble product. 1600 ppm Mo as ATM applied by incipient wetness from water and by using a pyridine solution followed by SCF extraction. All tests were under 1000 psig hydrogen (cold).

MICROBIAL HYDROGENATION OF COAL AND DIPHENYL METHANE

M.I.H. Aleem¹, D. Bhattacharyya², G.P. Huffman³, R.I. Kermode², M.V.S. Murty^{1,2}
H. Venkatachalam², and M. Ashraf¹
School of Biological Sciences¹, Department of Chemical Engineering², and
The Consortium for Fossil Fuel Liquefaction Science³
University of Kentucky, Lexington, Kentucky 40506

Keywords: Coal biohydrogenation, Microbial hydrogenation of diphenyl methane, H₂-transferring hydrogenase in *Sulfolobus* and *Desulfovibrio*.

ABSTRACT

The ability of *Desulfovibrio desulfuricans* and *Sulfolobus brierleyi* to catalyze the hydrogenation of coal and model compounds was investigated using Warburg-manometry in an atmosphere of H₂ without O₂. *D. desulfuricans* catalyzed H₂ uptake at a rate of 48 $\mu\text{mol/h}$ and 0.0701 $\mu\text{mol/h}$ with methylene blue (MB) and diphenyl methane (DPM) respectively, while the uptake rate by KCERL #91182 coal was 4.63 $\mu\text{mol/g coal/h}$. *S. brierleyi* was 8-12 times more effective catalyst yielding hydrogenation values of 619 $\mu\text{mol H}_2$ taken up/ $\mu\text{mol MB/h}$ and 0.5357 $\mu\text{mol H}_2$ taken up/ $\mu\text{mol DPM/h}$, while catalyzing the hydrogenation of coal at a rate of 44.1 $\mu\text{mol/g coal/h}$. The precipitated iron in the biodesulfurized coal by *S. brierleyi* was mainly in the form of super paramagnetic FeOOH as determined by the ⁵⁷Fe low temperature Mössbauer spectroscopy. These very fine paramagnetic particles (50-200 Å) exhibited good catalytic behaviour with higher liquefaction yield. Coals biotreated with *D. desulfuricans* also enhanced the chemical coal liquefaction yield by 5.67%.

INTRODUCTION

Bioprocessing of coal is emerging as a new technology for coal cleaning and coal conversion processes¹⁻⁷. Coal conversion under milder conditions continues to offer the potential for improved liquefaction of coal. The overall success of liquefaction may entail improved coal pretreatment, disposable catalysts, upgrading of coal liquids in terms of removal of nitrogen and organic sulfur, and novel hydrogen generation and utilization techniques. The development of these techniques as applied to the above objectives offers an alternative approach if appropriate microbial cultures and environmental conditions can be established. Our earlier work⁸⁻¹⁴ has demonstrated that under appropriate culture conditions, over 90% of the pyritic sulfur from coals can be removed by the mesophilic sulfur oxidizing autotrophic bacteria *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*, but these bacteria were incapable of removing organic sulfur. However, the thermophilic archaeobacterium *Sulfolobus brierleyi* was able to remove over 95% of the pyritic sulfur and over 30 % of the organic sulfur from the untreated coal when the cells of *S. brierleyi* were acclimatized.

The general reported area of biological conversion of substrate materials to higher quality fuels and chemicals are bioconversion of coal, lignite, and peat; hydrogen production by anaerobic microorganisms; and desulfurization. The aerobic biosolubilization of low-rank coal to polar water soluble products has been demonstrated¹⁵⁻¹⁸. The microbial desulfurization of oil-water emulsions and metabolism of dibenzothiophene has been demonstrated in our recent work¹². In addition, the in-situ formation of catalyst, FeOOH crystals on coal particles in the presence of *Sulfolobus brierleyi* for enhanced liquefaction has been observed in our laboratories^{10,14}. To our knowledge the direct microbial hydrogenation of untreated coal or the model compounds has not so far been demonstrated. We report here the results of our preliminary experiments.

MATERIALS AND METHODS

Organisms: Methods for growth and cell preparations for *sulfolobus brierleyi* have been described previously⁹. *Desulfovibrio desulfuricans* (ATCC strain No. 7757) was grown anaerobically in DSM medium #63 as described in the DSM catalogue (Deutsche Sammlung Von Mikroorganismen: German Collection of Organisms), Grisebachstrasse 8, D-3400 Göttingen, Germany. The cells were obtained by centrifugation (under anaerobic conditions) at 10,000 x g for 30 minutes and washed thrice with 0.05M phosphate buffer (pH 7.4). The cells were suspended in the same buffer and kept anaerobic at 4°C until use.

Hydrogenase Assay: The enzyme activity in *D. desulfuricans* was determined by Warburg manometry at 30°C and pH 7.4 and at 60°C and pH 2 in *S. brierleyi* with H₂ as the electron donor and methylene blue as the electron acceptor in an atmosphere of H₂ under anaerobic conditions. The reaction mixture had a total volume of 3 ml and contained 0.2 ml of 40% KOH in the center well of the reaction

flask to absorb any CO₂ released. Where applicable, the concentration of methylene blue or diphenyl methane was 4.2 and 6.5 mM respectively. Where indicated the concentration of untreated KCERL #91182 coal was 4.5%. The side arm of the Warburg flasks contained 0.3ml of the bacterial suspensions (approximately 3mg protein). The reaction flasks were shaken for 10 minutes under H₂ atmosphere for temperature equilibration before tipping-in the cells from the side arm. The H₂ uptake was recorded at 10-20 minute time intervals.

Mössbauer Spectroscopy: This technique provided a quantitative measurement of the reactions of pyrite and its transformations in Western Kentucky # 11 coal treated for biodesulfurization by *Sulfolobus brierleyi*. The techniques were essentially the same as described previously¹⁴. The coal liquefaction product yields (wt. %) determinations were performed by the University of Kentucky Center for Applied Energy Research using tetralin as a solvent, 800 psig H₂, and 427°C.

Samples for Mössbauer Spectroscopy: The samples of a Western Kentucky #11 coal were desulfurized using *Sulfolobus brierleyi* in a coal-water slurry aerated with air containing 10% CO₂.

RESULTS AND DISCUSSION

Comparative Rates of H₂-Uptake Catalyzed by *Sulfolobus brierleyi* and *Desulfovibrio desulfuricans*

Several aerobic and anaerobic bacteria possess hydrogenases but the ability of these microorganisms to catalyze the hydrogenation of coal and/or model compounds has not so far been reported. We have used an aerobic sulfur-oxidising thermoacidophilic archaeobacterium *Sulfolobus brierleyi* and an anaerobic sulfate-reducing mesophilic bacterium *Desulfovibrio desulfuricans*. Since both organisms possess hydrogenase enzymes, the data in Table 1 show that both organisms transferred reducing equivalents, e.g., electrons from H₂ to methylene blue, a conventional method used for measuring the hydrogenase activity in microorganisms. The comparative H₂ uptake rates catalyzed by the cells of *D.desulfuricans* and *S.brierleyi* were 48 and 619 µmoles of methylene blue reduced per hour respectively. The respective specific activities of the cellular enzyme were about 16 and 206 µmoles/h/mg protein indicating that the hydrogenase from *S.brierleyi* was about 13 times more potent than the hydrogenase from *D.desulfuricans*. While the hydrogenase of *S.brierleyi* was oxygen insensitive, the enzyme from *D.desulfuricans* might have been inactivated during the preparation of cells since oxygen is extremely toxic to the growth of *D.desulfuricans*. Thus the much lower activity of hydrogenase might not reflect its real potential. It is indeed significant, however, that the cells from both organisms were able to transfer H₂ to both diphenyl methane and untreated coal. Here again the specific activity of H₂-transferring enzyme e.g. hydrogenase was much lower in *D.desulfuricans* than that in *S.brierleyi*. The significant H₂ transfer rate catalyzed by *S.brierleyi* to the model compound diphenyl methane as well as to the untreated coal at 60°C is an important finding since the archaeobacterium is capable of not only removing sulfur from coal⁸⁻¹³ but is also able to catalyze coal hydrogenation which should lead to higher liquefaction yields.

Mössbauer Spectroscopy of the Biodesulfurized Coal: The behaviour and transformation of pyrite in the bioprocessed coal can be demonstrated by ⁵⁷Fe Mössbauer spectroscopy. The data is shown in Figure 1 for two biodesulfurized Western Kentucky #11 coals from two different desulfurization tests (tests K87 and 22) in which the pyritic content was significantly reduced by pretreatment with *S.brierleyi*. In the upper spectrum (K87) the pyritic sulfur was decreased from 3.3% to 0.1%, while in the lower spectrum (K22) the pyritic sulfur content fell from 1.2 to 0.1%. In both cases significant amounts of iron-bearing oxidation products were precipitated from the solution. Ferric sulfate (Jarosite) was the main oxidation product of pyrite (upper spectrum). In the lower spectrum, iron precipitation occurred when the CO₂ was shut off, and was primarily in the form of superparamagnetic FeOOH which is easily distinguished from pyrite and Jarosite in low-temperature Mössbauer spectra. Such paramagnetic phases have very fine particle sizes (50-200 Å) and therefore, they exhibit good catalytic behaviour during liquefaction as indicated by data in Table 2 where the liquefaction conversion of the parent coal for run 22 was compared to that of biodesulfurized samples taken before and after the disruption of the CO₂ flow which caused the precipitation of superparamagnetic FeOOH. The higher conversion percentage of liquefaction for sample 22B compared to sample 22A indicates the catalytic nature of FeOOH which raised the conversion percentages of the desulfurized coal back to about that of the untreated pyrite-rich coal. Hence the knowledge of the forms of iron in bioprocessed coal provided by Mössbauer spectroscopy can provide strategies for optimization of sulfur reduction and other conversion technologies.

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Table 1
Comparative Rates of Hydrogen Uptake Catalyzed by
Sulfolobus brierleyi and *Desulfovibrio desulfuricans*

Organism	Substrate	Hydrogen uptake $\mu\text{mol/g coal/h}$
<i>S.brierleyi</i>	Coal	44.10
<i>D.desulfuricans</i>	Coal	4.63
$\mu\text{mol}/\mu\text{mol DPM}^*/\text{h}$		
<i>S.brierleyi</i>	DPM	0.5357
<i>D.desulfuricans</i>	DPM	0.0701
$\mu\text{mol}/\mu\text{mol MB}^{**}/\text{h}$		
<i>S.brierleyi</i>	MB	619
<i>D.desulfuricans</i>	MB	48

See 'Materials and Methods' for experimental conditions.

* - DPM - Diphenyl methane ** - MB - Methylene blue

Table 2
Liquefaction product yields (wt.%) of biodesulfurized coal
Tetralin, 800 psig H₂ (ambient)

	385°C			427°C		
	Parent Coal	22A ^a	22B ^b	Parent Coal	22A ^a	22B ^b
Gas	2	12 ^c	3	4	5	6
Oil	10		8	39	41	39
Asphaltene	22	24	20	32	29	33
Preasphaltene	39	21	36	13	10	12
IOM ^d	28					
Conversion	72	57	67	87	84	90

^aBioreacted, before FeOOH precipitation. ^bBioreacted after FeOOH precipitation

^cGas and oil not determined separately for this sample. ^dInsoluble organic matter or residue.

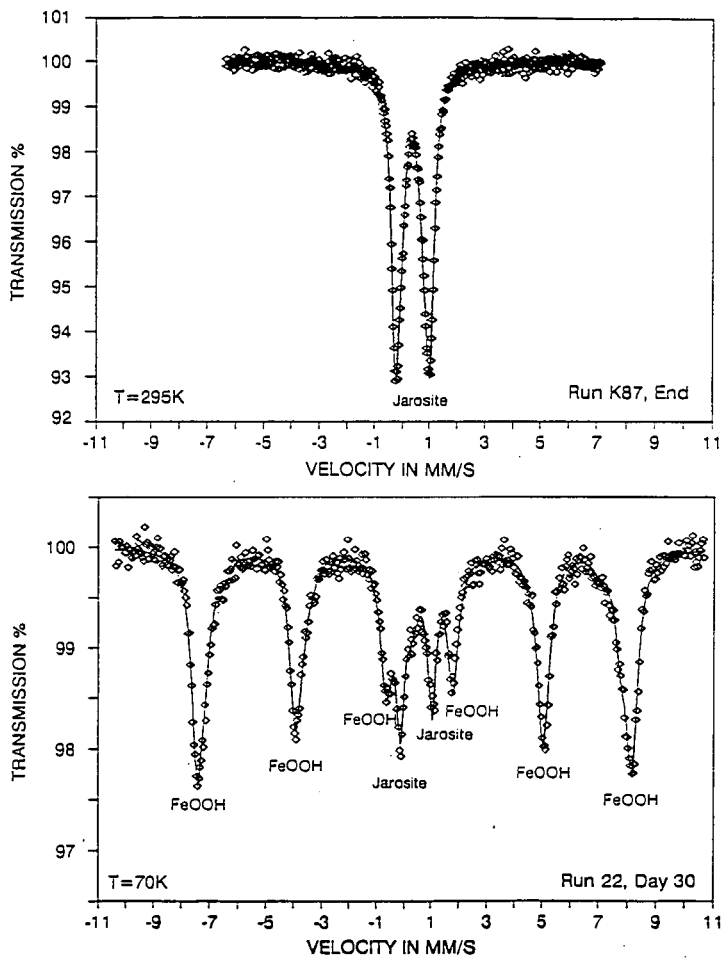


Fig. 1. Mössbauer spectra of biodesulfurized samples of Western Kentucky coals.

AGGLOMERATION OF LOW-RANK COAL AS A PRETREATMENT FOR DIRECT COAL LIQUEFACTION

G. A. Robbins, R. A. Winschel, C. L. Amos
CONSOLIDATION COAL COMPANY
Research & Development
4000 Brownsville Road
Library, PA 15129

Keywords: Oil Agglomeration, Direct Liquefaction, Coal Cleaning

INTRODUCTION

Oil agglomeration is an effective technique for recovering and deashing coal fines. In addition to conventional uses of oil agglomeration, certain features make it attractive as a pretreatment for coal liquefaction. The small coal grind size required for liquefaction may improve the release of mineral contaminants from the coal. These sizes may be more easily handled by oil agglomeration than by conventional cleaning methods. The use of process-derived oil eliminates the additional cost of the agglomerating oil. It also has been shown that pyrite is not effectively removed from coal fines by oil agglomeration (1), since its surface is readily coated by oil. Pyrite is recognized as a liquefaction catalyst (2) and retention of this mineral can be beneficial in liquefaction processes. The economic incentive for lowering the ash content of liquefaction feedstocks result from: 1) the potential of down-sizing or eliminating deashing equipment, 2) improved yields from more efficient ash rejection, 3) reduced erosion/abrasion of equipment, and 4) slightly improved organic throughputs resulting from reduced ash inventory in the system.

The goal of this work was to determine if coal liquefaction process oils are effective in cleaning low-rank coals (subbituminous and lignite) by agglomeration. Previous work of this nature in this laboratory has been limited to characterization of oils for the agglomeration of bituminous coal (3). The work reported here has been described in complete detail in DOE reports (4,5). The coals tested consisted of three subbituminous coals, a Texas lignite, and a bituminous coal (for comparison and establishing operating conditions). The agglomerating oils included petroleum-derived No. 2 diesel fuel and No. 6 fuel oil, two Lummus Integrated Two-Stage Liquefaction (ITSL) distillates from bituminous coal runs, and a Wilsonville ITSL distillate from a run with Texas lignite. Past bench-scale work at ConsoI using similar equipment has provided results which were scalable to commercial operation at 40 tph (6).

EXPERIMENTAL

The coals used in the tests are described in Table 1. All coals were run-of-mine; several were supplied previously ground. The agglomerating oils and surfactant are described below, and selected properties are shown in Table 2.

- Diesel Fuel No. 2 - Purchased locally.
- Fuel Oil No. 6 - API gravity 13, low sulfur grade.
- Lummus Run 3LCF9 - A sample of the 500 x 850°F distillate second-stage product produced in October 1982 at the Lummus ITSL PDU during a period of run 3LCF9 using Old Ben No. 1 Mine (Indiana V) coal.
- Lummus Run 3LCF7 - A composite sample of the 850°F distillate portion of the second-stage heavy-oil product made during Run 3LCF7 of the Lummus ITSL PDU with Old Ben No. 1 Mine (Indiana V) coal.

- Wilsonville Run 255 - A sample of the recycle distillate inventory (V-1074) from 5/2, 4, 6, 7/88 during Run 255, made while the plant processed Martin Lake (Texas) lignite, nominal b.p. about 650 x 1000°F.
- Cresylic Acid No. 83 Black (Merichem Company; Houston, Texas).

Agglomeration experiments were performed in a cylindrical stainless steel vessel (Figure 1). The drive motor is rated at 1700 rev/min. The test procedure is shown in Figure 2. A cylindrical heating mantle was used when tests were made above ambient temperature.

Inversion, or phase separation, was manifested by a distinct change in the sound produced by the mixing action and by changes in color and texture at the surface of the slurry. In some tests, additional oil was added to increase agglomerate size. The reject material was dried at 105°C to constant weight (at least two hours), and then weighed and ashed at 800°C to constant weight (three hours or more).

The agglomerates were allowed to air-dry until they were visibly dry (16-48 hours). Moisture and ash were determined on the agglomerated products.

Organic recoveries, ash rejections, and ash balances were determined as shown below:

Organic Recovery =

$$\left[1 - \frac{\text{mass of dry reject} - \text{mass of ash in reject}}{\text{mass of MAF coal} + \text{mass of oil}} \right] \times 100\% \quad (1)$$

Ash Rejection =

$$\left[\frac{\text{mass of coal ash charged} - \text{mass of ash in product}}{\text{mass of coal ash charged}} \right] \times 100\% \quad (2)$$

Ash Balance =

$$\left[\frac{\text{mass (ash) in agglomerates} + \text{mass (ash) in dry reject}}{\text{mass of coal ash charged}} \right] \times 100\% \quad (3)$$

Though not determined, oils were assumed to be ash-free for the calculations. The ash balance calculations (Table 3) do not account for any water-soluble ash. However, elemental analyses of products, rejects and water-soluble ash from two runs were used to obtain complete ash elemental balances and rejection selectivities.

RESULTS AND DISCUSSION

General

Results are reported for nineteen successful agglomeration tests performed with six coal samples (lignite through hvAb) and five different agglomerating oils. Unsuccessful trials are described in another report (4), but not presented here. Table 3 gives the conditions and results of all the successful agglomeration trials (i.e., those runs which produced agglomerates). Organic recoveries ranged from 85% to 100% and were greater than 98% for all the low-rank coal tests. Ash rejections ranged from -1% to 72%. The low-rank coal tests gave ash rejections of up to 56%. Ash balances were 73% to 108% (not accounting for water-soluble rejected ash).

After initial work with a variety of coals, efforts were concentrated on Texas lignite and Wyodak subbituminous coal. Of ten tests conducted with Texas lignite, four produced agglomerates with a petroleum oil and one produced agglomerates with a coal liquefaction oil (fortuitously, the lignite-derived oil). Ash rejection with

No. 6 fuel oil ranged from 39 to 56%, while the lignite-derived oil gave 39% ash rejection. Organic recoveries were always greater than 98% and ash balances ranged from 73% to 100%.

Wyodak subbituminous coal was successfully agglomerated with three different coal liquefaction oils and one petroleum-derived oil. Ash rejections with the coal liquefaction oils ranged from 6 to 19%. With No. 6 fuel oil, ash rejections were 1 to 15%. Organic recoveries were about 98% and ash balances ranged from 88 to 102%.

A chart of the coal/oil combinations used appears below.

CHART OF COAL/OIL COMBINATIONS TESTED FOR AGGLOMERATION

Oils	COALS					
	Texas Lignite	Wyodak (Coarse) Subbit.	Wyodak (Fine) Subbit.	Rosebud Subbit.	Kemmerer Subbit.	Pittsburgh Seam Bitum.
Diesel Oil	-	--	----	---	+	++
No. 6 Fuel Oil	++++	+	+	0	0	0
Lumms 3LCF9 Oil	-	+	++	++	+	+
Lumms 3LCF7 Oil	--	+	0	0	0	0
W'ville Run 255	+-	0	+	0	0	0

- = No agglomeration
 + = Agglomeration
 0 = No test performed with this combination

The low-rank coals are ranked Kemmerer > Wyodak fine = Wyodak coarse = Rosebud > Texas lignite in terms of ease of agglomeration. Kemmerer coal appears to be equivalent to Pittsburgh seam coal in ease of agglomeration, but the Kemmerer coal had a very low initial ash content and thus gave low ash rejections. There was no difference evident in the response to agglomeration of -200 mesh (finely ground) compared with -28 mesh (coarsely ground) Wyodak coal. Some mineral liberation effect may have been evident, since the coarser grind size gave a maximum ash rejection of 10%, compared to 19% for the finer grind size.

The oils appear to be ranked No. 6 fuel oil > the three coal liquefaction oils > diesel oil in agglomerating ability. Every coal liquefaction oil successfully agglomerated one of the Wyodak coals, but no data are available to directly compare them in agglomeration of other coals. It appears that appropriate agglomeration temperatures for the oils are: room temperature for diesel oil and the two Lumms oils; 38°C for Wilsonville oil; and 54°C for No. 6 fuel oil. Note that no systematic attempt was made to optimize the agglomeration temperature for each oil. Precedent for effective temperatures for No. 6 fuel oil and the two Lumms oils was established in earlier work using bituminous coals (3).

Effects of Promoter and pH

It was reported elsewhere that cresylic acid promoted the agglomeration of lignite (2). Cresylic acid was used as a surfactant or additive in five runs, with the following effects: 1) it was necessary for the agglomeration of the lignite with the lignite-derived oil at the conditions tested (Run 35), 2) it appeared to improve ash rejection (Wyodak subbituminous coal (Runs 23 and 36), but not lignite), 3) it improved the slow kinetics of agglomeration of the lignite, and 4) it lowered the ash balance. In Run 30 (no cresylic acid), the induction period for phase inversion

was about 40 minutes. In Run 33, with cresylic acid, the induction period was about 6 minutes. Obviously, this has significant consequences for any commercial application of this technology. The lignite is the only coal that was successfully agglomerated which showed any significant kinetic limitation in agglomeration; the other coals had induction periods of two minutes or less. In Run 35, the induction time was about 12 minutes. A similar run made without cresylic acid was terminated after one hour without agglomeration. These results indicate that cresylic acid speeds up the agglomeration of the lignite.

In several agglomeration trials, the pH was adjusted by the addition of various reagents prior to oil addition, without effect in most cases. The one exception was Run 31, in which the slurry pH was adjusted from 6.8 to 2.0 by the addition of HCl. The run was otherwise identical to Run 30. The lower pH resulted in faster agglomeration (phase inversion after 9 minutes instead of 40 minutes), higher ash rejection (56% vs 46%) and a lower ash balance (73% vs 96%). This is very similar to some of the effects caused by the addition of cresylic acid. Note that cresylic acid had no effect on slurry pH.

Elemental Balances

It is necessary to analyze the rejected water (filtrate) to close ash and ash elemental balances. Complete ash and elemental balances were obtained from one agglomeration run with Martin Lake (Texas) lignite (Run 35) and one run with Clovis Point (Wyodak seam) subbituminous coal (Run 36).

Liquid and solid samples were analyzed in duplicate by ICP-atomic emission spectroscopy. Average elemental results were used to calculate a mass balance for ash and for each element. The balances for ash and ash elements relative to the feed coal (i.e., feed coal has 100% of each component) are shown in Figure 3. Ash elemental analyses for the feed coals are given in Table 1. Ash balances shown are on an SO₃-containing and an SO₃-free basis. SO₃ retention is an artifact of the ashing process. The SO₃-free ash balances are a better representation of the coal mineral balances. In coal liquefaction, the fate of the mineral matter is more important than the fate of the ash. For the Wyodak coal test (Run 36), ash rejection was 19.2% (whole-ash and SO₃-free ash bases). For the lignite test (Run 35), the ash rejection was 38.7% (SO₃-containing basis) and 44.3% (SO₃-free basis). This suggests that SO₃-free ash rejections may be uniformly greater than the whole-ash rejections reported for the lignite tests. This results from the selective retention of Ca (and hence SO₃) in the product from the lignite run. Except for ash and ash SO₃, all other components yield the same rejection results when treated on either basis. Overall ash balances were 93 to 96%. Ash balances for individual elements ranged from 89 to 113% for Run 35 and from 84 to 125% for Run 36. The balance for Na₂O was the highest (113% and 125%) observed. Other elements gave balances lower than 106%, with most in the 89 to 96% range. Sodium was greatly reduced in the product agglomerates, and most of it ended up in the water.

Shown in Figure 4 is the selectivity for rejection of each of the ash elements, computed on an SO₃-free basis, for each of the runs. Selectivity was obtained by:

$$\text{Selectivity for Rejection} = \frac{\text{wt oxide in product}}{\text{wt oxide in feed}} \times \frac{\text{wt ash in feed}}{\text{wt ash in product}} \times 100\% \quad (4)$$

The values thus obtained are less than 100% for components selectively rejected from the product (i.e., rejected to a greater degree than the overall ash) and greater than 100% for components selectively retained in the product. It is evident that Al₂O₃, TiO₂, Fe₂O₃, CaO and MgO were selectively retained in the products and SiO₂ and Na₂O were selectively rejected from the products in both runs, although retention of Fe₂O₃, CaO and MgO was small in Run 36 (Wyodak). K₂O was rejected and P₂O₅ retained in Run 35 (lignite), but no selectivity for either was observed in Run 36

(Wyodak). Also, ash SO_2 was retained in Run 35 (lignite), but showed no selectivity in Run 36 (Wyodak). The fates of the ash elements are clearly illustrated in Figures 3 and 4.

CONCLUSIONS

This work demonstrated that low-rank coals can be cleaned by agglomeration with coal liquefaction oils. To the authors' knowledge, this is the first time cleaning of low-rank coal by agglomeration with coal liquefaction oils has been demonstrated. It is expected that agglomeration performance, e.g., ash rejection and induction time could be further improved by additional testing.

The Texas lignite is readily cleaned by oil agglomeration, with ash rejections of 50% and higher possible. The Wyodak and Kemmerer coals used here appear less amenable to cleaning by agglomeration, the best ash rejections being about 15 to 20%. The Kemmerer coal may have been particularly difficult to deash because of its low original ash content (3.6%). Rosebud coal showed little or no cleanability under the conditions used; however, the conditions may have been less than ideal.

Each of the coal liquefaction oils tested agglomerated at least one of the Wyodak coals. The apparent ranking of the coals in ease of agglomeration (not necessarily deashing) is Pittsburgh Seam = Kemmerer > Wyodak fine = Wyodak coarse = Rosebud > lignite. The apparent ranking of the oils in agglomerating ability (but not deashing) is fuel oil No. 6 > the three coal liquefaction oils > diesel oil.

Ash elemental results show some form of iron, a potential liquefaction catalyst, is selectively retained in the agglomeration products. also selectively retained are the elements Ti, Ca and Mg. Sodium, a potential poison to supported catalysts is selectively rejected. The concentrations of all ash elements, even those that were selectively retained, are lower in the agglomerated product than in the feed coal.

ACKNOWLEDGMENTS

The Wilsonville oil sample and the low-rank coals were provided by Dr. Charles Cantrell from the Wilsonville pilot plant laboratory. Lummus-Crest, Inc. supplied the Lummus oils. Fuel oil was provided by Boswell Oil Co. of Dravosburg, Pennsylvania. Cresylic acid was provided by the Merichem Company, Houston, Texas. This work was funded by the U.S. Department of Energy under contract Nos. DE-AC22-84PC70018 and DE-AC22-89PC89883.

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TABLE 1
FEED COAL IDENTIFICATION AND ANALYSES COAL/OIL AGGLOMERATION

Designation	Code	Mine	Seam	State	Apparent Rank	Moisture wt %, as det.	Ash, wt % MF
Pittsburgh Seam	MC	--	Pittsburgh	WV	hVAb	1.39	26.15
Wyodak (Coarse)	WC	Clovis Point	Upper & Lower Wyodak	WY	sub.	24.6	8.35
Wyodak (Fine)	WF	Clovis Point	Upper & Lower Wyodak	WY	sub.	20.8	8.41
Kemmerer	KC	Kemmerer	Adeville	WY	sub.	17.9	3.55
Texas Lignite	TC	Martin Lake	Wilcox	TX	lig.	25.9	15.4
Rosebud	RC	Rosebud	Rosebud	MT	sub.	22.98	7.41

Major Elements, Oxide wt % of Ash (As Determined)										
SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Mn ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Unac-counted
<u>Texas Lignite</u>										
50.09	13.51	1.10	4.45	13.12	3.14	1.00	0.62	0.15	13.36	-0.54
<u>Wyodak (Fine)</u>										
28.88	13.32	0.70	6.46	22.60	3.80	1.67	0.25	0.70	22.06	-0.44

Notes and Code: Samples WC, WF, KC, TC and RC supplied by the Wilsonville pilot plant laboratory.
Sample MC supplied by Consol.
Sample WF supplied as -200 mesh.
Samples MC, WC, KC, TC and RC supplied as chunks, ground at Consol to -28 mesh.
Ash elemental analyses were not obtained from coals MC, WC, KC and RC.

TABLE 2
SPECIFIC GRAVITIES AND ¹H-NMR PROTON DISTRIBUTIONS OF AGGLOMERATION OILS AND ADDITIVE

Oil Designation	Specific Gravity	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
No. 2 diesel oil	0.842	2.9	6.0	4.8	7.7	13.5	39.0	26.1
No. 6 fuel oil	0.899	5.3	2.3	7.1	6.4	13.3	44.8	20.8
Lumus 3LCF9	1.041	20.3	6.6	16.4	9.0	20.0	16.6	11.1
Lumus 3LCF7	1.022	13.2	6.6	15.8	0.6	23.2	19.5	13.2
Wilsonville Run 255	0.931	7.5	5.2	13.6	8.8	19.2	29.5	16.2
Cresylic acid	-	1.9	24.5	7.4	35.5	4.5	12.5	5.3

TABLE 3

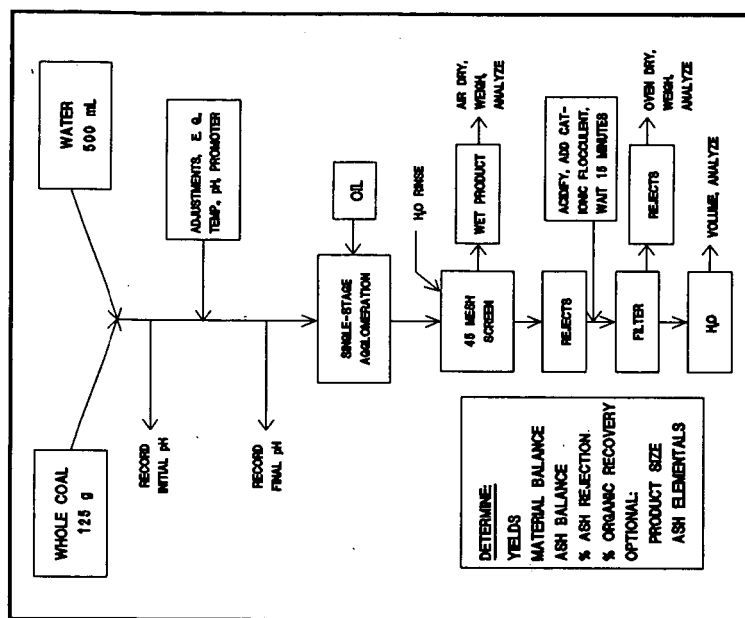
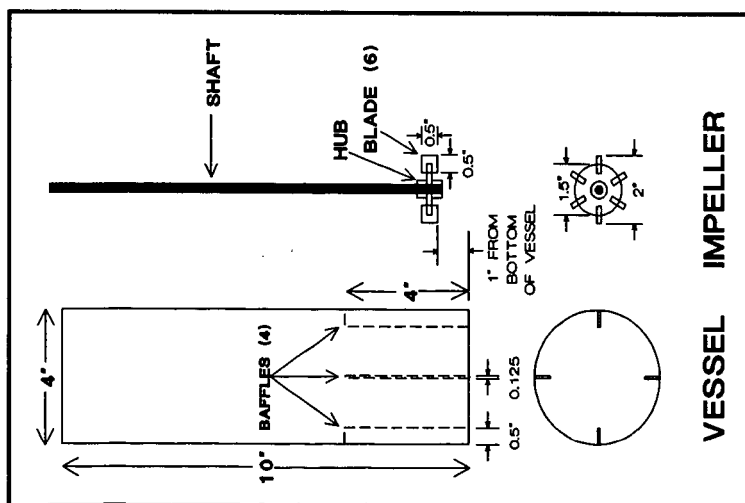
CONDITIONS AND RESULTS OF SUCCESSFUL AGGLOMERATION TRIALS

Run No.	Feed Coal	Agglom. Oil	Slurry pH, Initial/ Final (Agent)	Notes	Added Oil at Phase Inver- sion/ Total, ml.	Product				MF Reject		Organic Recov., %	Ash Rejec- tion, %	Ash Bal., %
						Moisture, wt %	MF Ash, wt %	Air Dry Mass, g	Mass, g	Ash, wt %				
5	Pittsburgh	Diesel	6.1/10.0 (NaOH)	-	3/14	6.58	9.12	105.32	30.76	55.7	86.7	72.2	81.0	
6	Pittsburgh	Diesel	6.1/8.5 (NaOH)	1	3/30	8.75	8.97	135.18	38.92	60.9	88.7	65.7	107.9	
8	Pittsburgh	3LCF9	8.4/8.4	-	10/35	3.24	8.37	119.99	38.90	50.2	84.8	69.9	90.7	
9	Kemmerer	3LCF9	7.3/7.3	-	8/14	14.2	2.83	134.38	0.71	64.2	99.8	10.4	102.1	
11	Kemmerer	Diesel	7.3/7.3	-	8/22	10.3	2.62	126.65	1.18	81.1	99.8	18.3	107.9	
20	Rosebud	3LCF9	6.3/6.3	-	7/25	8.56	6.05	130.16	0.11	52.9	100.0	-0.9	101.7	
21	Rosebud	3LCF9	6.3/6.3	-	7/15	9.69	6.20	122.33	0.18	71.5	100.0	4.0	97.8	
22	Wyodak coarse	3LCF9	5.2/5.2	-	13/25	9.83	6.02	131.60	0.18	62.0	99.9	9.2	92.2	
26	Wyodak coarse	3LCF7	5.2/5.2	-	10/13	18.2	6.62	131.23	0.61	67.3	99.8	9.7	95.5	
27	Wyodak coarse	#6 fuel	5.3/5.3	-	9/10	10.7	7.50	115.97	0.29	90.0	100.0	1.3	102.0	
23	Wyodak fine	3LCF9	5.1/5.1	-	15/45	8.56	5.48	156.40	0.52	74.0	99.9	5.9	98.8	
29	Wyodak fine	#6 fuel	5.2/5.2	-	10/25	21.7	5.66	159.03	1.14	77.4	99.8	15.4	95.3	
36	Wyodak fine	3LCF9	5.1/5.1	2	21/21	12.8	5.76	133.89	2.43	25.4	98.4	19.2	88.2	
37	Wyodak fine	Run 255	5.1/5.1	2	20/20	12.0	6.06	129.65	2.09	30.8	98.7	17.0	90.8	
28	Texas lignite	#6 fuel	7.1/7.1	-	20/23	19.7	8.19	132.20	6.09	91.4	99.5	39.0	100.0	
30	Texas lignite	#6 fuel	6.8/6.8	-	15/15	11.4	7.77	111.56	6.59	91.8	99.4	46.2	96.3	
31	Texas lignite	#6 fuel	6.8/2.0 (HCl)	-	15/15	28.6	6.67	131.32	4.44	93.2	99.7	56.2	72.9	
33	Texas lignite	#6 fuel	6.7/6.7	2	15/15	22.9	8.73	121.87	5.73	81.6	98.9	42.5	90.3	
35	Texas lignite	Run 255	6.7/6.7	2	16/16	11.2	8.78	112.13	5.54	78.6	98.7	38.7	91.8	

*Runs conducted at ambient temperature with diesel, 3LCF7 and 3LCF9 oils. Runs conducted at 38°C with Run 255 oil and 54°C with fuel oil #6.

Note 1: 25 g coal added after final oil addition.

Note 2: Promoted by 1.87 g cresylic acid.



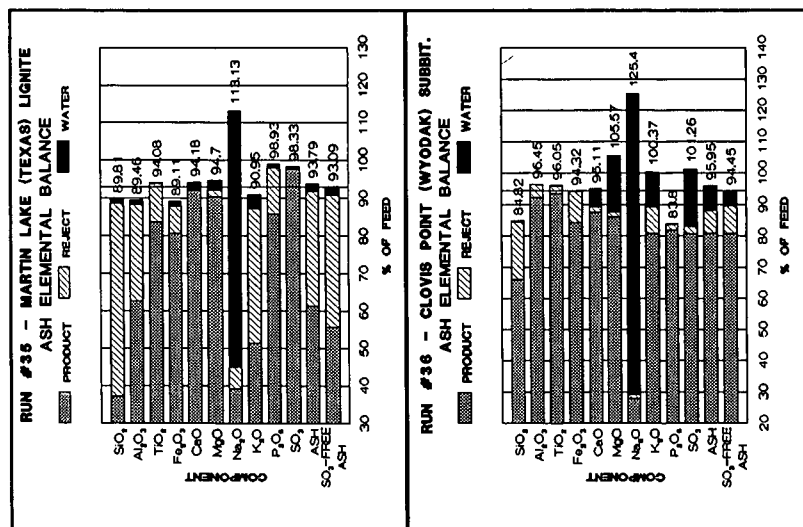


Figure 3. Ash Elemental Balance for Selected Runs.

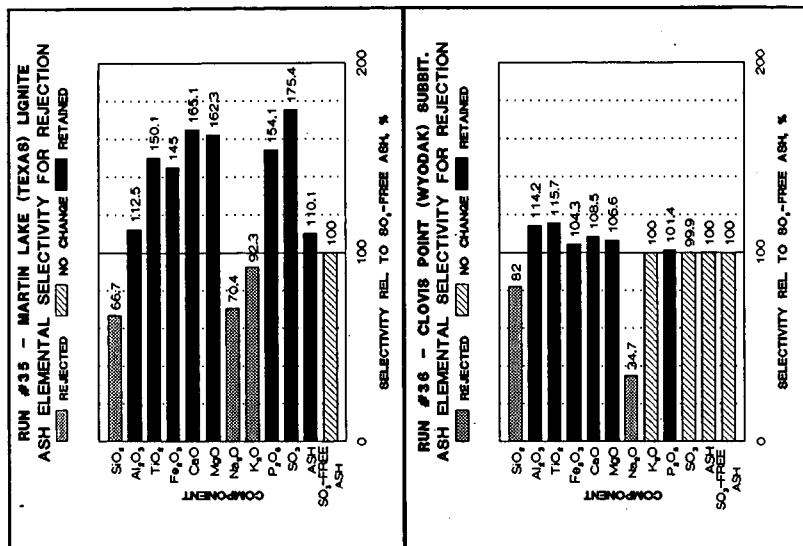


Figure 4. Ash Elemental Selectivity for Rejection for Selected Runs.

COAL BENEFICIATION: PROCESS DEVELOPMENT FOR LIQUEFACTION

Cronauer, Donald C. and Swanson, April J.
Amoco Oil Company, Naperville, IL 60566

ABSTRACT

Research was undertaken to evaluate techniques for removing mineral matter and unreactive components from coal for subsequent liquefaction. A sample of Burning Star Mine, Illinois No. 6 seam, bituminous coal was crushed, sieved, and gravity separated. The yields of fines (-60 mesh), float (1.40 gravity) and sink fractions were 30%, 46% and 24%, respectively. The ash levels were 14.9%, 6.5% and 18.3%, respectively. In the treatment of Martin Lake Texas lignite, the yield of fines was only 14%, but it contained 24% ash. To remove metal salts of organic acids in the lignite, the coarse fraction (+60 mesh) was treated with sulfurous acid and then gravity separated. The ash levels of the treated float and sink fractions were 5.6% and 39.3%, respectively. The overall recovery of the float fraction was 62%. Fractions of these coals were liquefied in a two-stage, bench-scale unit. The preferred feeds for high coal conversion were the float fractions. Both the sink and -60 mesh fine fractions should be rejected and used as fuel. However, in the case of Illinois No. 6 coal, the sink fraction gave a low-boiling product, presumably due to catalytic activity of the remaining mineral matter which had a high iron content.

INTRODUCTION

Several papers¹⁻⁵ have reported that coal liquefaction conversion is related to the concentration of macerals in the feed coal. Specifically, vitrinites convert well; liptinites liquefy well, but somewhat slowly; and inertinites liquefy only to a limited extent.

Coal beneficiation provides a means to separate the more reactive macerals from the mineral matter and less reactive macerals. Minerals can often be liberated by sufficient size reduction, and the unreactive maceral fusinite, which is charcoal-like, breaks into small particles during crushing and is concentrated in the fine fractions. Maceral density increases in the order liptinite < vitrinite < inertinite. Therefore, a portion of the inertinites along with minerals can be concentrated in the high-density fractions isolated by "sink/float" gravity separation.

In addition to mineral matter, low rank coals contain high levels of organic acids that bond cations. These consist of alkali and alkaline earth cations attached to carboxylates. Mochida et al.⁶ have shown that pretreatment of lignites with 0.4M HCl significantly increased conversion during liquefaction. We use sulfurous acid because of its low cost, easy recoverability, and less corrosive nature. Sulfurous acid hydrolyzes organic acid salts present as exchangeable ions in low rank coals. The resulting metal bisulfites are washed from the coal and subsequently precipitated.

The second aspect of this paper deals with the liquefaction of treated coal samples. These are liquefied at conditions that are representative of those in use at the Advanced Coal Liquefaction Facility located in Wilsonville, AL. Descriptions of this process have been published.⁷⁻⁹

In this facility, unconverted solids are separated from liquefaction product using the ROSE-SR process of Kerr-McGee Corp. The mineral-rich "ash concentrate" stream carries along a sizable amount of heavy liquefaction product¹⁰⁻¹¹ which is either lost, used as fuel, or gasified. If the level of mineral matter and unreactive coal in the liquefaction feed stream is low, organic losses also are low.

The objectives of our work were to prepare samples of beneficiated Illinois No. 6 bituminous coal and Martin Lake, Texas, lignite and to evaluate the liquefaction behavior of the various coal fractions using a two-stage, continuous flow unit.

EXPERIMENTAL

Fresh samples of Illinois No. 6 seam coal (Consolidation Coal Co. Burning Star Mine) and Martin Lake lignite (courtesy of Texas Utilities Electric, Dallas, TX) were obtained. Portions were pulverized under nitrogen and subsequently stored at 40°F.

Coal liquefaction solvents were obtained from the Wilsonville facility. They were derived from the liquefaction of similar coals (the same coal in the case of Illinois coal and Black Thunder subbituminous coal-derived product for the lignite runs.). Analyses are given in Table I.

Bulk samples of beneficiated coal were prepared at Hazen Research, Inc., Golden, CO. The Hazen facility includes coal crushing and wet screening units and a closed circuit sump-pump-cyclone unit. Water and magnetite media were added to the feed sump, the resulting slurry was pumped to the cyclone, and cyclone products were recycled to the sump. The specific gravity of each charge was determined and the amount of magnetite adjusted accordingly. The 8x60 mesh coal was added to the media at a ratio of about 1:5. When stable flow conditions were established, timed samples of the cyclone overflow and underflow were collected. The product samples were wet-screened at 60 mesh to remove the magnetite. Recovered coal was filter-pressed and dried under nitrogen at room temperature at Amoco.

A portion of the 8X60 mesh lignite was agitated with sulfur dioxide saturated water. The liquid was decanted, and the resulting lignite was flushed with water. The lignite was then wet screened with additional water flush prior to sampling and gravity separation.

Pilot plant-scale liquefaction runs were made in a two-stage unit that operates in a once-through, continuous mode with regard to H₂, solvent, and coal, and in a batch mode with regard to catalyst. Each stage functions as a continuous, stirred-tank reactor (CSTR), as previously described.¹⁴

Presulfided Amocat-1C catalyst was used in both reactors. Operating temperatures in the two stages were 790°F and 740°F, and nominal residence times were 1.5 and 1 hour, respectively. Feed slurries with Illinois No. 6 coal were 33/67 coal/solvent, and those with Martin Lake lignite were 25/75.

Catalyst was lined out for about one week. Subsequent samples were run for about three days. A solvent only period was also included.

Coal conversion is defined in terms of tetrahydrofuran (THF), toluene, and hexane soluble material as determined by Millipore filtration. Modified ASTM distillations were carried out with subsequent to atmospheric pressure. Products were analyzed for C, H (Leco), N (AutoKjeldahl), S (X-ray fluorescence), metals (Inductively Coupled Plasma spectroscopy/ICP).

Because resid is present in the feed solvent and is generated from the liquefaction of the lignite, the yield of resid from the lignite is calculated as a difference between the measured level in the product and that observed in the reference solvent only period. A "negative" yield may result if less resid is recovered than determined in the solvent only run.

RESULTS

Coal Beneficiation:

Illinois No. 6 Coal: The results of the beneficiation of fresh Illinois No. 6 coal are summarized in Figure 1. Coal crushing and screening resulted in a 70% recovery of 8X60 mesh coal, designated "coarse". The "fines" (-60 mesh) could not be handled by heavy media beneficiation. A sample of the coarse coal was sink/float beneficiated at a specific gravity of 1.35. This resulted in a 66/34 (dry coal basis) split between the overflow and underflow of the cyclone. On the basis of coal feed, the product yields were: 30% fines, 46% overflow (float), and 24% underflow (sink).

Results of elemental analyses of the recovered fractions are shown in Table II. The feed coal contained about 12% ash. The levels of ash in the fines and sink fractions were high at about 15% and 18%, respectively. The float fraction contained 6.5% ash. This latter value is typical of that observed for such treatment of Illinois coal.¹² High levels of sulfur in the fines and sink fractions were likely due to high levels of pyrite in these fractions. The fines had a marginally low H/C ratio when compared to the other samples (0.79 vs. 0.82); this may have been due to a high level of inertinites.

Martin Lake Lignite: As shown in Figure 2, the yield of fines from crushing was only 14%. An additional 2% was generated during the sulfurous acid treatment step. Sink/float separation of the treated lignite was done at a gravity of 1.40. The resulting split between overflow and underflow was 76/24 on a dry coal basis. The overall product distribution was: 16% fines, 62% overflow (float), and 22% underflow (sink).

Analyses of lignite samples are given in Table III. The fines fraction had a very high ash level (24% vs. 15% in the feed); therefore, this fraction might better be used as fuel and not as a liquefaction feedstock. Sulfurous acid treatment of the coarse fraction resulted in about a 30% reduction of ash. From previous studies¹³ with this lignite, the 30% ash reduction was due primarily to the partial removal of alkali and alkaline earth metals. Gravity separation of the treated coarse fraction resulted in a sizable improvement in ash levels (5.6% vs. 39.3% for the float and sink fractions, respectively). However, further inspection of the sink fraction indicated that magnetite had not been effectively removed. The correct ash level in the sink fraction should be about 31%.

As also shown in Table III, there was an increase in sulfur and oxygen contents in the treated samples in comparison with the feed lignite. About 1 to 2% SO_2 was retained in the lignite as a result of treatment.

Liquefaction of Illinois No. 6 Coal Samples:

Differences were observed in conversion, resid yield, and hydrogen consumption from the liquefaction of the coal fractions, as shown in Table IV. The sink fraction produced low conversion to THF solubles, indicative of a high inertinite content. However, liquid product from the sink fraction was of very high quality, containing virtually no resid. Conversely, product from the float fraction was heavy, containing twice as much resid as product from the reference coarse coal. Therefore, sink/float beneficiation of Illinois No. 6 coal apparently does more than just change the level of unconverted coal and ash. The removal of some of the mineral components, which probably had catalytic properties, affected the upgrading aspects of liquefaction.

The effect of beneficiation is also indicated by the level of hydrogen consumption. An internal catalyst was present in the sink fraction, as indicated by hydrogen consumptions of 6.0% for the sink fraction and 4.7% for the float fraction. Iron was the likely internal catalyst as shown from the metals analyses in the unconverted coal solids (Table V). The sink sample was enriched in Fe, and to a lesser extent Ca.

Liquefaction of Martin Lake Lignite Samples:

Conversion of sulfurous acid-treated lignite to THF solubles was higher than that of the untreated lignite (Table VI), but the product contained much more resid. The second lignite liquefaction run was made only with samples of sulfurous acid treated lignite. Surprisingly, conversions of both the sink and float samples were lower than that of the coarse treated material that was used as their feedstock; see Table VII. The treated sink fraction gave only 6% conversion, which is consistent with a high inertinite level, as found in analogous laboratory-scale samples.¹²

The yield of resid from sulfurous acid-treated lignite was significantly higher than from untreated lignite, 12% vs. -6%, respectively. The difference between resid yields is not as great as shown, because contributions from solvent conversion changed throughout the run. However, there was at least 10% more resid produced from the treated lignite.

High yields of distillable product, defined as 975°F- liquids, were obtained from the treated float and sink fractions. In fact, no resid was recovered from processing the treated float fraction. There was a negative yield in the case of the sink fraction, indicating that some of the resid present in the feed solvent was being converted in addition to that generated from the lignite. The sink fraction was heavily contaminated with magnetite, which apparently acted as an upgrading catalyst.

CONCLUSIONS

Beneficiation of Illinois No. 6 coal using sequential size selection and gravity separation was effective in obtaining an improved coal liquefaction feedstock. However, there were both positive and negative effects. Ash and inertinite removal by rejection of the sink fraction would decrease liquid losses in the solids separation step. Offsetting this, internal mineral matter catalyst is also rejected thereby resulting in heavier liquefaction products. Sulfurous acid treatment and sink/float beneficiation of Martin Lake lignite is clearly beneficial. Ash levels in the lignite were reduced, conversion was slightly increased, and an all-distillate product was generated.

ACKNOWLEDGMENTS

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FIGURE 1

IL NO. 6 BENEFICIATION PROCEDURE

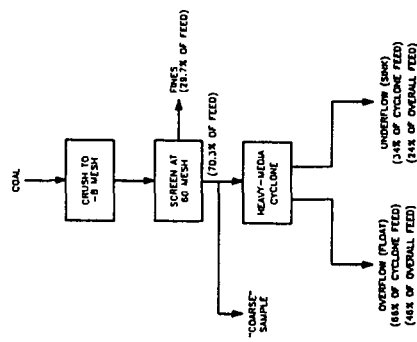


FIGURE 2

LIGNITE BENEFICIATION PROCEDURE

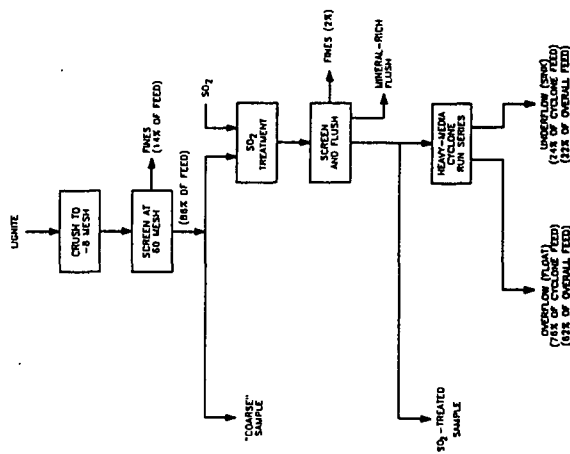


TABLE I
SOLVENT ANALYSES

WILSONVILLE RUN	257	258
WILSONVILLE COAL	IL. NO. 6	BLACK THUNDER
ELEMENTAL ANALYSES, Wt%		
C	89.26	89.54
H	8.83	8.28
N	0.57	0.80
S	.08	.05
O	1.26	1.33

Distillation, Wt%

IBP-650°F	0.36	8.83
650-975°F	55.78	93.70
975°F	43.86	37.46

Solubility, Wt%

THF INSOLUBLES	0.12	0.09
TOLUENE INSOLUBLES	1.07	1.31
HEXANE INSOLUBLES	7.96	15.33

TABLE II
ANALYSES OF BENEFICIATED IL NO. 6 COAL SAMPLES

ULTIMATE ANALYSES (DRY BASIS)			
	FEED	FINES	COARSE OVERFLOW (FLY)
CARBON	69.0	66.8	70.0
HYDROGEN	4.7	4.4	4.8
NITROGEN	1.5	1.5	1.4
SULFUR	3.5	3.8	3.4
ASH	11.9	14.9	10.7
OXYGEN (DIFF)	9.4	8.6	9.7

TABLE III
ANALYSES OF BENEFICIATED
MARTIN LAKE LIGNITE SAMPLES

ULTIMATE ANALYSES (DRY BASIS)			
	FEED	FINES	COARSE SO ₂ TREATED COARSE
CARBON	63.3	56.8	64.4
HYDROGEN	4.5	4.0	4.6
NITROGEN	1.2	1.2	1.3
SULFUR	1.5	1.6	1.5
ASH	14.6	23.6	13.1
OXYGEN (DIFF)	14.9	12.8	15.2

TABLE IV

LIQUEFACTION OF DENSITY BENEFICIATED
IL. NO. 6 COAL

COAL SAMPLE	COARSE	FLY	SINK
CONVERSION	94.6	94.7	92.7
C ₁ -C ₃ HYDROCARBON	3.2	6.5	6.0
C ₄ -360°F	9.5	5.4	12.5
360-650°F	38.4	29.5	35.8
650-975°F	23.6	26.5	27.7
975°F RESID	9.3	18.6	0.5
HYDROGEN CONSUMPTION	5.6	4.7	6.0

TABLE V

METALS IN UNCONVERTED COAL
(WEIGHTS ARE REPORTED RELATIVE TO ALUMINUM)

COAL	COARSE	FLOAT	SINK
Ca	0.33	0.14	0.39
Fe	2.07	1.57	2.72
Hg	0.08	0.07	0.08
Na	0.05	0.05	0.04
K	0.22	0.23	0.23
Ti	0.05	0.05	0.04
V	0.00	0.01	0.00
Zn	0.01	0.01	0.02
Mn	0.00	0.01	0.00
Cr	0.01	0.01	0.01
Ni	0.00	0.01	0.00

TABLE VII

COMBINED WATER/SO₂-BENEFICIATION AND DENSITY
BENEFICIATION

LIGHTS SAMPLE	WATER/SO ₂ -BENEFICIATED	
	TREATED FEED	FLOAT
CONVERSION	91.0	86.4
C ₁ -C ₃ HYDROCARBON	8.6	10.2
C ₄ -360°F	9.6	7.9
360-650°F	29.5	37.9
650-975°F	9.7	14.7
975+°F RESID	16.5	0
HYDROGEN CONSUMPTION	6.4	6.4
		8.4

TABLE VI

WATER/SO₂-BENEFICIATED MARTIN LAKE LIGNITE

LIGHTS SAMPLE	UNTREATED	WATER/SO ₂ -BENEFICIATED
CONVERSION	84.7	91.3
C ₁ -C ₃ HYDROCARBON	7.3	6.2
C ₄ -360°F	13.2	14.1
360-650°F	33.5	33.1
650-975°F	24.7	9.6
975+°F	-6.3	12.0
HYDROGEN CONSUMPTION	7.4	7.4

RESULTS FROM UNTREATED FINES WERE INCONCLUSIVE BECAUSE THE PILOT PLANT OPERATED AT 0.5 RELATIVE SPACE VELOCITY DUE TO PUMPING DIFFICULTIES.

CTSL™ CATALYTIC TWO-STAGE LIQUEFACTION COUPLED WITH COAL CLEANING

Alfred G. Comolli
Edward S. Johanson
Sudhir V. Panvelker
Gabriel A. Popper

Hydrocarbon Research, Inc.
100 Overlook Center, Suite 400
Princeton, New Jersey 08540

Key words: CTSL, Liquefaction, Beneficiation

Introduction

The overall objective of the CTSL process, which has been under DOE sponsored Bench-Scale development since 1983, is to achieve higher distillate yields, better quality products and to lower production and capital costs in relation to existing direct coal liquefaction technologies.

CTSL is a two-stage direct liquefaction process using close-coupled ebullated-bed reactors with the first stage operating at milder temperatures than the second stage (see Figure 1). Cobalt or nickel molybdenum on alumina catalysts are used to produce an all distillate slate of products with low sulfur and nitrogen contents. The lower temperature first stage promotes hydrogenation of the coal derived oils and of the recycled solvent prior to hydrocracking and additional heteroatom removal in the second stage.

Efforts have been underway to improve economics of the process by improving yields while reducing erosion and solids separation requirements through cleaning and beneficiation of the coal prior to liquefaction. Various techniques have been examined and tested in HRI's Bench-Scale unit. The Bench-Scale unit consists of a two-stage continuous ebullated-bed reactor system with on-line fractionation and optional on-line fixed-bed hydrotreating. At a nominal capacity of 50 pounds of coal per day, this size unit clearly defines process chemistry of a CSTR system with operations in a batch mode with respect to catalysts. Scale-up is on a 1/1 basis to the next larger PDU operations size on a selected equilibrium catalyst activity basis.

HRI has examined various modes of beneficiation/cleaning and evaluated them in both single and two-stage processing. Some of the techniques evaluated were: Heavy Media Cleaning, Electrostatic Precipitation, Oil Agglomeration of Pulverized Coal, Oil Agglomeration of Micronized Coal and Chemical Leaching.

Program

Present direct coal liquefaction studies at HRI are sponsored by DOE under a three year contract from 1988 to fiscal 1992. The baseline coal for cleaned and beneficiated coal studies has been Illinois #6 Burning Star coal with a typical analysis as shown in Table 1. The evaluations of heavy media and electrostatically cleaned coals occurred in a preceding contract in 1986, the oil agglomeration tests were recently completed in 1990.

Objective

The specific objectives of these studies were to quantify the reactivity differences resulting from beneficiation and to determine the processing advantages resulting in solid separation and product handling.

Studies

Five samples of Illinois #6 Burning Star Mine coal cleaned by different techniques were evaluated in continuous two-stage ebullated-bed bench-scale operations to examine their liquefaction behavior. The five cleaning techniques were: heavy media density separation, electrostatic precipitation, chemical leaching and oil agglomeration of pulverized and micronized coal. Operations and results of the cleaned coals were compared directly with a sample of conventionally cleaned (washed) coal from the mine and run at near identical conditions.

The coal samples were prepared at other laboratories briefly as follows: Heavy Media cleaned coal was cleaned at the Bituminous Coal Research facility in Monroeville, PA using magnetite as the dense phase with a total recovery of about 67 W% of the feed coal. Coal cleaned and beneficiated by electrostatic precipitation was prepared in a proprietary process by AED, Advanced Energy Dynamics of Natick, Mass. using a vertical belt separator feeding -70 mesh dried coal supplied by HRI. Recovery was 47% with a possible of 85% using a finer grind and rotary apparatus. The coal prepared by the "Ash Lite", Resource Engineering, Inc. leaching method also used -70 mesh coal from HRI and was prepared in Waltham, Mass. with a reported carbon yield of over 90% and an ash reduction to 3.6%. A major change was noted with an increase in the chlorine content of the coal from 0.06 W% to 1.8 W% after cleaning.

A coal sample was prepared at Homer City, PA by Bechtel under contract to DOE using spherical agglomeration with heptane and asphalt while feeding coal pulverized to less than 50 mesh. The coal was supplied with a hard asphalt content of 1.9 W% and 6.8 W% moisture and fed to the bench unit as received.

A fifth cleaned and beneficiated coal was prepared in Syracuse, NY by the proprietary "OTISCA" coal process and supplied as a 35% slurry in water. This coal is also cleaned using light solvents and a fine micronized coal of 5 micron median diameter. This was the only coal sample that required special handling to remove the water to low levels prior to liquefaction.

Maceral analysis were obtained on each of the coals in addition to ash and sulfur and other heteroatoms to determine the degree of beneficiation and effects on liquefaction and reactivity of the coals in a catalytic ebullated-bed system. A 1/32" extrudate catalyst of alumina promoted with nickel molybdate was used in all the sample evaluations and start-up oil was a Wilsonville derived heavy distillate from Illinois Coal. The operating conditions were 2500-2800 psig system pressure, reaction temperatures of 750/800°F, space velocity of 45 lbs/hr/ft³ of settled catalyst and oil/coal ratio of 1.1/1 except for the OTISCA coal at about 2 to 1.

Results and Discussion

The coal prepared by REI using the "Ash Lite" process showed lower reactivity than other samples when screened on a microautoclave scale and failed due to a high pressure drop after operating 13 hours in the continuous bench-scale apparatus. As a result, only minimal data was obtained on this sample.

Each of the other coals operated smoothly showing enhanced reactivity when compared with untreated, mine washed coal. In the OTISCA coal/water slurry tests coals were compared on the same micronized size and water concentration basis.

The proximate and petrographic analysis of the coal samples are presented in Table 2. In each cleaning technique, the coals are beneficiated by a reduction in the inerts and fusinite. A summary of normalized yields and performance data are presented in Table 3. Comparisons are made with mine washed coal and with unagglomerated micronized coal.

Coal Conversion - The coal conversion follows the decrease in inertinite and ash contents showing higher conversion ranging from 89 to 96 W%. The lower coal conversions for the micronized coal studies may be attributed to the use of 10% lower slurry coal concentration and subsequent lower residence time.

Resid Conversion - Residual oil or 975°F* conversion (basis = 100-unconverted coal and residual oil) is considerably improved as the ash content is reduced, ranging from 82 to 92% for the lowest ash coal.

Distillate Yields - Distillate yields follow a similar pattern, ranging from 66 to 69% for the uncleaned coals to 71 to 76 W% MAF for the cleaned and beneficiated coals. A bar chart comparison is shown in Figure 2 with the spherical oil agglomerated cleaned coal showing the highest yield at 76.2 W% of MAF coal. The electrostatically cleaned coal falls outside the pattern; this may be the result of some oxidation as shown by high sulfate sulfurs.

Product Quality - The quality of the oils produced was generally enhanced by cleaning, showing higher hydrogen contents and lower heteroatom levels. Table 4 illustrates the improved quality of the 500-650°F product as obtained with coal cleaned by spherical agglomeration.

Conclusions

- Coal cleaning and beneficiation (reduction of inert organic matter) by methods studied herein produces higher coal conversion and distillate yields in ebullated bed reaction systems.
- The improved productivity is accompanied by lower solid removal requirements and a probable lower erosion rate in let-down valves and lines.
- The highest yields were obtained with the heavy media cleaned and spherical oil agglomeration products.
- Residual oil conversion appears to correspond directly with ash content (see Figure 3) which may be the result of reducing catalyst poisons.

Economic studies are currently underway to determine the product cost benefit of using cleaned coal techniques. The two methods currently under consideration based on the results of this study are heavy media and spherical oil agglomeration cleaning.

Acknowledgments

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TABLE 1
FEED COAL ANALYSES
ILLINOIS NO. 6 BURNING STAR MINE

Feed Designation	(Run-of-Mine)	(Agglomerated)
<u>Ultimate Analysis (W%, Dry Basis)</u>		
Carbon	65.12	74.75
Hydrogen	4.57	5.23
Sulfur	3.80	2.90
Nitrogen	1.33	1.53
Ash	15.21	4.62
Oxygen (by difference)	9.97	10.97
<u>Sulfur Forms (W%, Dry Basis)</u>		
Sulfate	0.12	0.05
Pyrite	1.84	0.59
Organic	1.74	2.23
<u>Mineral Analysis of Ash (W%, Ignited)</u>		
Silica, SiO ₂	49.50	38.40
Alumina, Al ₂ O ₃	19.62	18.00
Titania, TiO ₂	0.90	0.99
Ferric Oxide, Fe ₂ O ₃	20.52	28.02
Lime, CaO	4.08	4.96
Magnesia, MgO	1.04	1.10
Potassium Oxide, K ₂ O	1.76	1.70
Sodium Oxide, Na ₂ O	0.85	1.30
Sulfur Trioxide, SO ₃	1.09	4.11
Phosphorous Pentoxide, P ₂ O ₅	0.31	0.31
Undetermined	0.33	1.11

TABLE 2
CLEANED, BENEFICIATED COAL ANALYSIS

Ultimate, W% Dry	Mine Washed	Heavy Media Cleaned	Electrostatic Cleaned	Chemical Cleaning	Oil Agglom. Pulverized	Oil Agglom. Micronized	Micronized Unagglom.
Carbon	70.4	73.9	74.3	74.0	74.8	75.9	69.3
Hydrogen	4.5	4.9	4.7	4.8	5.2	5.2	4.5
Nitrogen	1.4	1.5	1.5	1.9	1.5	1.5	1.3
Sulfur	3.6	2.8	3.1	3.2	2.9	2.7	3.5
Ash	10.6	5.8	4.9	3.6	4.6	3.5	10.6
Oxygen (Diff.)	9.5	12.1	11.4	10.8	11.0	11.3	10.7
<u>Sulfur Forms, W% Dry</u>							
Sulfate	0.12	0.25	0.30	0.01	0.05	0.07	0.11
Pyrite	1.8	0.5	0.7	1.1	0.6	0.6	1.3
Organic	1.7	2.1	2.0	2.3	2.2	2.1	2.0
<u>Petrographic, V%</u>							
Total Reactives	88.2	91.5	92.6	90.1	91.9	84.5 ⁽¹⁾	81.1 ⁽¹⁾
Total Inerts	11.8	8.5	7.4	9.9	8.1	15.5	19.9
Fusinite	1.9	0.3	0.5	0.8	3.3	NA	NA

(1) Performed at a different laboratory

TABLE 3
YIELDS AND PERFORMANCE OF CLEANED COALS

	Mine Washed	Heavy Media Cleaned	Electrostatic Cleaned	Oil Agglom. Pulverized	Oil Agglom. Micronized	Micronized Unagglom.
<u>Yields, W% MAF</u>						
C ₁ -C ₃	5.9	6.2	6.7	7.3	8.3	5.6
C ₄ -390°F	17.1	19.0	18.9	22.3	21.6	18.1
390-650°F	32.9	35.7	32.4	33.1	39.6	29.0
650-975°F	19.2	18.6	20.1	17.3	11.9	19.2
975°F*	8.3	8.3	9.5	4.9	1.4	7.5
<u>Performance, W% MAF</u>						
Coal Conversion	93.0	96	96.2	95.4	93.3	89.3
975°F* Conv.	84.7	87.8	86.6	90.2	91.9	82
C ₄ -975°F* Yield	69.2	73.3	71.4	76.2	73.1	66.3
Hydrogen Consumption	7.1	7.5	7.3	7.0	7.9	6.7

TABLE 4
DETAILED COMPARISON OF
SPHERICAL AGGLOMERATED COAL

Coal Feed	Agglomerated		R-O-M
Ash in Coal Feed, W%	4.62	4.62	15.21
NiMo Catalyst Age. Lb Coal/Lb Cat.	106	233	319
<u>Yields, W% MAF Coal</u>			
C ₁ -C ₃ Hydrocarbon Gases	7.9	7.6	8.9
C ₄ -975°F Liquids	75.0	76.2	68.8
975°F* Residual Oil	2.0	5.1	7.1
H ₂ O, NH ₃ , H ₂ S, CO _x	17.1	13.8	16.4
Hydrogen Consumption	7.7	7.4	7.4
Coal Conversion	94.5	95.4	93.7
Product (Recycle) Resid. Conc., W%	16.6	26.7	31.0
<u>Properties, 500-650°F Product</u>			
Hydrogen, W%	11.57	11.39	11.08
Nitrogen, W%	0.11	0.10	0.13
Sulfur, W%	<0.01	<0.01	<0.02

HRI EBULLATING-BED CATALYTIC TWO-STAGE COAL LIQUEFACTION (CTSL) PROCESS **SIMPLIFIED FLOW PLAN**

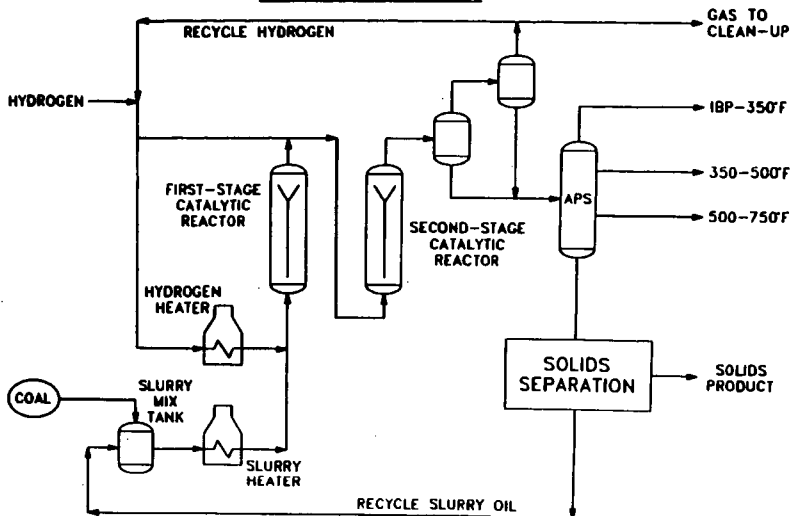


FIGURE 1

**FIGURE 2
CLEANING METHOD EFFECT
ON DISTILLATE YIELDS**

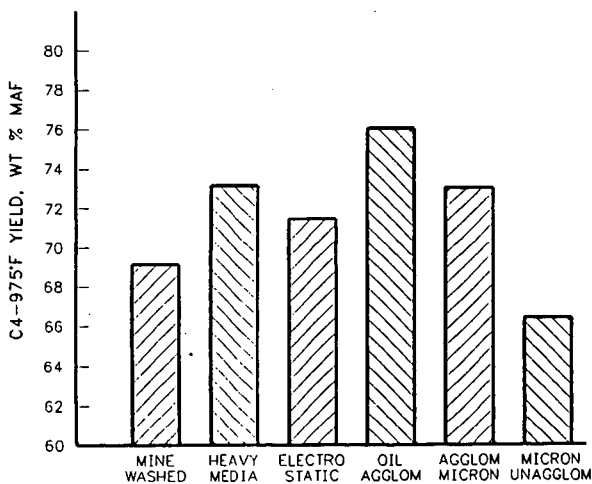
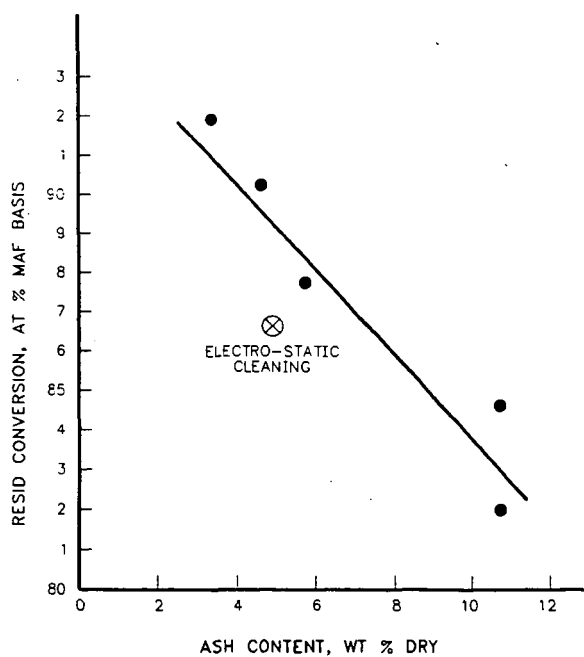


FIGURE 3
ASH EFFECT ON RESIDUAL
OIL CONVERSIONS IN EBULLATED BEDS



PRECONVERSION TREATMENTS OF LOW-RANK COAL

John R. Rindt, Melanie D. Hetland, Randal S. Sauer,
William M. Sukalski, and Leslie W. Haug
University of North Dakota Energy and Environmental Research Center
Box 8213, University Station
Grand Forks, ND 58202

Keywords: direct liquefaction, low-severity preconversion treatments

INTRODUCTION

Coal can be converted to very high yields of oil using a two-stage processing approach. To obtain even higher yields, however, it may be necessary to control the processing conditions to which coal is subjected in a manner that significantly reduces the role that repolymerization, recombination, and/or coking reactions play in the conversion process. Improvements in conversion and distillate yields may be possible if the conversion stage is subdivided into a low-severity preconversion treatment and a noncatalytic conversion step. This multistep first stage could produce a completely soluble product, theoretically increasing the effectiveness of the second-stage catalytic upgrading.

EXPERIMENTAL METHODS

A three-year program, funded by the U.S. Department of Energy under Contract Number DE-FC21-86MC10637, is underway to investigate various preconversion treatments and methods of increasing the conversion of LRCs to soluble material during the first stage. As a first step, low-severity preconversion treatments were screened to evaluate their impact on the direct liquefaction of Indian Head lignite. Several schemes were devised, and an experimental matrix was developed to screen them. Screening was carried out using the 20-cm³ microreactor system and the 1-gallon hot-charge autoclave system. Six pretreatment schemes were tested in each system. For comparative purposes, two single-step tests were performed in the microreactor system using H₂ as the reductant: one at 372°C and the other at 423°C.

Testing proceeded in two steps. The first step consisted of the preconversion treatment at the matrix-specified temperature for 60 minutes. In the case of the microreactor system, half of the microreactors were removed after preconversion treatment and the products analyzed. The remaining six duplicate microreactors were charged with hydrogen and treated at approximately 410°C for 20 minutes. When the autoclave system was used, a sample was removed for analysis following the preconversion treatment. The remaining material was then reacted with H₂ at nominally 410°C for 20 minutes. The higher than usual, first-stage temperatures were used during these studies in order to highlight the differences between the products.

RESULTS AND DISCUSSION

It should be kept in mind that, for this discussion, liquefaction is considered to be comprised of two steps: the first stage and the catalytic upgrading (second) stage. Only preconversion treatment and the first stage were studied during this work; catalytic upgrading of the products was not studied.

Microreactor Tests

Preconversion Treatment Screening Tests The conversions to THF solubles that were achieved by the six preconversion treatment schemes screened in the microreactor system are presented in Table 1. The table presents the conversions to THF-soluble material after the preconversion treatment and after the first-stage processing. Initial discussion will focus on the conversion following the first-stage processing.

The first reactant combination consisted of Indian Head lignite, A04 (coal-derived anthracene oil) solvent, and H_2 . Conversions achieved with this combination after preconversion treatment and subsequent first-stage processing ranged from 37.1% at a preconversion treatment temperature of 175°C to 67.4% at a temperature of 110°C. This combination was compared with the second scheme, which consisted of lignite, A04 solvent, and CO. It was hypothesized that the nascent hydrogen produced during the water/gas shift reaction ($CO + H_2O \rightarrow CO_2 + 2H \cdot \rightarrow CO_2 + H_2$) would be used more readily by the coal than hydrogen added as the reducing gas. Differences were noted in the conversion to THF solubles of the two schemes. These differences increased as the preconversion treatment temperature increased, so that a marked difference was noted at 250°C. At this temperature, the conversion for the A04/ H_2 combination was 63.4% and the conversion for the A04/CO combination was 79.1%. The water/gas shift reaction is more active at 250°C than it is at the lower treatment temperatures. Therefore, it appears that the nascent hydrogen was more readily used by the coal than the hydrogen that was added as the reducing gas.

The third combination tested consisted of lignite, cresylic acid (CA1), and CO. This combination was chosen to determine if some of the material that physically prohibits the reaction of the coal with the hydrogen could be extracted with CA1. The results did not indicate that this was the case, as the CA1/CO scheme resulted in lower conversions at each temperature than did the A04/CO combination. For example, at 175°C the CA1/CO combination resulted in a 26.4% conversion, while the A04/CO scheme's conversion was 40.7%. At 250°C, the CA1/CO conversion was 72.1%, compared with 79.1% conversion for the A04/CO scheme.

The fourth combination made use of lignite, CA1, CO, and sodium. The use of sodium as a promoter for the addition of hydrogen to the coal structure was evaluated in this combination. A substantial increase in conversion (from 72.1% to 92.9%) was noted when sodium was present in the system at 250°C. Based upon the limited data available, it appears that sodium did promote the addition of hydrogen to the coal structure.

The fifth combination made use of lignite and tetralin in the absence of a reducing gas to determine if hydrogen transferred directly from the solvent to the coal. This approach was quite successful at the lowest preconversion treatment temperature (110°C), achieving an 87.5% conversion. A relatively low conversion of 56.4% was noted at 250°C, presumably due to the absence of CO as a reducing gas and its part in the water/gas shift reaction.

The sixth combination was performed using lignite, tetralin, and CO to determine if the hydrogen-donating solvent requires a reducing gas in order for the hydrogen transfer to take place. At 110°C, the tetralin-only system achieved an 87.5% conversion, while the tetralin/CO combination achieved a 48.8% conversion. The results were reversed at 250°C, where the tetralin/CO combination achieved a conversion of 86.3% and the conversion of the tetralin-only scheme was 56.4%. Presumably the water/gas shift reaction was a factor in the higher conversion of the tetralin/CO combination at 250°C.

Single-Step Processing Table 2 presents the conversions achieved during single-step processing using the microreactor system. The tests were performed for comparison to the first six preconversion treatment screening tests. The average conversion to THF solubles using tetralin as the solvent was approximately 90% during single-step processing at 430°C. This is slightly better than the conversion attained at a preconversion treatment temperature of 250°C for the tetralin/CO combination or that achieved by the tetralin alone at a treatment temperature of 110°C. It does not appear that the preconversion treatment had a significant impact on the conversion of lignite to THF-soluble material when tetralin was used as the solvent.

The conversion to THF solubles achieved using A04 as the solvent at a processing temperature of 430°C probably averaged near 60%, as the 76.4% conversion seems to be

out of line with the other two values. A conversion of 60% during single-step processing was somewhat less than that attained after preconversion treatment at either 110° or 250°C, but is greater than that achieved after treatment at 175°C. As was the case with tetralin, it does not appear the preconversion treatment had a significant impact on the conversion of lignite to THF-soluble material when A04 was the solvent.

When CA1 was used as the solvent during single-step processing at 430°C, the resulting conversion was approximately 45%. This value is considerably worse than that achieved by preconversion treatment at either 110° or 250°C. This seems to indicate that preconversion treatment can improve the conversion of lignite to THF-soluble material when a cresylic acid solvent is used.

Autoclave Tests

The remaining six preconversion screening tests (the seventh through twelfth combinations) were performed in the 1-gallon, hot-charge autoclave system at a nominal temperature of 175°C. The data obtained during these tests are presented in Table 3. Most of the tests were performed to investigate the addition of H₂S to the combinations of solvents and reducing gases tested in the first six (microreactor) tests. Previous studies indicated that the use of H₂S catalyzes the reactor walls. Relative to the reactor volume, the wall effects due to this catalysis are sufficient to skew the results when the testing is performed in the microreactor system. Although the use of H₂S also catalyzes the walls of the autoclave system, the effects on the products are less pronounced due to the larger volume-to-surface area ratio, resulting in a truer indication of the effects of H₂S on a given reaction.

The seventh combination tested consisted of lignite, tetralin, and argon. The resulting conversion of 78.9% was compared with that of the eighth combination, which consisted of lignite, tetralin, argon, and H₂S as a reaction promoter. The presence of H₂S resulted in a conversion of 85.3%. The use of H₂S in this instance appears to improve the conversion of lignite to soluble material.

The ninth combination tested consisted of lignite, A04, argon, and H₂S and resulted in a conversion of 80.0%. The conversion was not as high as that achieved using tetralin and H₂S. The fact that A04 is not as good a hydrogen-donating solvent as tetralin may account for the difference in conversion.

The tenth combination made use of lignite, A04, CO, and H₂S to evaluate both the reaction-promoting capabilities of H₂S in the presence of a reducing gas and the effect of H₂S on the water/gas shift reaction. The resulting conversion of 83.0% was higher than the 80.0% achieved by the A04/argon/H₂S combination. This may indicate that the presence of a reducing gas slightly improves the conversion and/or that the H₂S enhances the water/gas shift reaction.

The eleventh combination consisted of lignite, CA1, CO, and H₂S. This scheme was not especially successful when compared with the other combinations. A conversion of 70.9% was achieved, less than the 83.0% achieved using A04 solvent. This same trend was noted in the data from the microreactor tests.

The final test was the primary combination test using A04 and H₂, and it achieved the lowest conversion of all combinations tested in the autoclave system, a 60.7% conversion of coal to THF-soluble material.

Trends Noted After Preconversion Treatment Only

Conversions to THF solubles were determined for most of the tests following the preconversion treatment. These values are presented in Tables 1 and 3. When comparing the conversions after preconversion treatment only, it is possible to

discern some major differences between the reactions taking place with the different combinations.

At treatment temperatures of 175°C or less, tests performed using A04 as the solvent always had a negative conversion to soluble material of nominally -10% following preconversion treatment. In other words, at that point in the processing, the reaction had actually polymerized some of the feed slurry. In the presence of A04, upgrading of the insoluble organic matter (IOM) to soluble resid and distillable oils must take place primarily during the first stage.

Conversion to THF solubles after preconversion treatment using CA1 was positive with only one exception. This indicates that the CA1 solvent begins its conversion at very low-severity conditions, possibly through solubilization of portions of the coal.

At 250°C, the conversion to THF-soluble material was nearly as high after preconversion treatment as it was after liquefaction processing. This is most likely due to the effect of the water/gas shift reaction at this temperature. As would be expected, tests involving CO at this temperature exhibited the highest levels of conversion to THF solubles.

Comparison of Product Slates of Autoclave Tests

Evaluation of the data should not be restricted to conversion to THF-soluble materials, but should also include the product slates when possible. Due to sample size, product slates could be determined for the products of the autoclave tests only. Tables 4 and 5 present the product slates after preconversion treatment and first-stage processing, respectively. The values are presented in terms of moisture- and ash-free (maf) coal fed to the system. The product slates of the preconversion treatments will be examined first.

The tests using the light-oil solvents (tetralin and CA1) resulted in the conversion of more coal to soluble resid than the tests performed with A04 as the solvent, as shown in Table 4. The coal was probably solubilized by these solvents during the pretreatment. For the tests performed using A04, a significant portion of the coal remained as insoluble organic matter (IOM) after the preconversion treatment was completed. Table 6 presents the solvent recoveries realized during these tests. As the table shows, the solvent recoveries for the tetralin and CA1 tests were lower after the preconversion treatment than the A04 recoveries, indicating that these solvents reacted with the coal during the preconversion treatment while the A04 did not. As would be expected, the lack of gas production indicates that very little gasification took place during this pretreatment step.

Other observations can be made when the various preconversion treatment schemes are compared based upon the product slates of the first-stage processing, as given in Table 5.

An increase in CO₂ production indicated that more decarboxylation took place during the tetralin/argon test than during the tetralin/argon/H₂S test. The presence of H₂S resulted in the production of less soluble resid and IOM and more light oils and water from the coal. The H₂S seemed to aid in the conversion of the soluble resid present in the coal. During the test performed without H₂S, soluble resid equal to approximately 60 wt% of the maf coal fed to the reactor was produced at the expense of the production of light oils.

The liquid product of the A04/Ar/H₂S combination contained more IOM and soluble resid than the product of the tetralin/Ar/H₂S test. This is probably due to the heavier nature of the solvent and the reactions which took place during the preconversion treatment step.

When CO was used with the A04/H₂S combination instead of argon, more CO, CO₂, and soluble resid were produced from the coal, while less of the coal remained as IOM. The A04/CO/H₂S combination required less of the coal-derived light oils for upgrading to soluble resid than the A04/argon/H₂S scheme. However, more of the coal went to middle oil production in the presence of argon than CO. In other words, the test performed with argon resulted in the upgrading of more of the coal to lighter products than the test with CO.

When CA1 was used as the solvent instead of A04 in the CO/H₂S scheme, CO was consumed rather than produced by the coal. All of the soluble resid present in the coal as well as some of that present in the CA1 solvent after preconversion treatment were upgraded to water and light oils. This was significant when compared to the nonproduction of light oils during the test with A04. However, nearly twice as much of the coal remained as IOM at the end of the test with CA1 as at the end of the test using A04. It appears that CA1 upgrades the solubilized material better than A04, but the lighter nature of the solvent does not permit the upgrading of the heavier insoluble material.

Comparison of the A04/H₂ combination to the A04/CO/H₂S combination reveals that less gas was produced during the H₂ test. The H₂ test failed to upgrade approximately 40% of the coal, which appears in the product as IOM. Of the coal which was upgraded during the A04/H₂ test, approximately half went to soluble resid and half went to middle oils. By comparison, the majority of the upgrade during the A04/CO/H₂S test was to soluble resid with very little coal upgrading to distillable oils.

When comparing the A04/H₂ and the A04/argon/H₂S combinations, the argon/H₂S was more successful in upgrading the coal to soluble resid. Similar quantities of coal went to middle oils for both tests, but considerably more of the coal remained as IOM when treated with H₂.

CONCLUSIONS

- In the presence of A04, upgrading of IOM took place primarily during the first stage, whereas when CA1 was used as the solvent, conversion began at very low-severity conditions.
- Nascent hydrogen from the water/gas shift reaction was more readily used than hydrogen from the reducing gas.
- If any material physically prohibits conversion, it was not extractable with cresylic acid solvent.
- Sodium appeared to promote hydrogen addition to coal.
- Hydrogen-donating solvents were the most successful at converting coal to soluble material.
- The use of H₂S as a reaction promoter appeared to enhance conversion and result in generally lighter liquids than those produced when H₂S was not present.

It appears that conversion of lignite to THF-soluble material can be improved through the use of specific, solvent-dependent preconversion treatment. Small increases in conversion are possible with A04 solvent, while larger differences are possible when CA1 is the solvent of choice. This indicates that preconversion treatment can prevent some of the retrograde reactions that take place when CA1 is used as the solvent.

TABLE 1
RESULTS OF PRETREATMENT SCHEMES TESTED IN THE MICROREACTOR SYSTEM

Run Numbers	Pretreatment Temperature	Solvent	Reducing Gas ^a	Additive	% Conversion to THF Solubles	
					After Pretreatment	After 1st Stage ^b
T380, T381	110°C	A04 ^c	H ₂	-- ^d	-5.9	67.4
		A04	CO	--	-8.4	66.3
		CA1 ^e	CO	--	9.5	* ^f
		CA1	CO	Na ^g	*	63.9
		Tetralin	--	--	-9.0	87.5
		Tetralin	CO	--	*	48.8
T378, T379	175°C	A04	H ₂	--	-7.4	37.1
		A04	CO	--	-11.0	40.7
		CA1	CO	--	7.2	26.4
		CA1	CO	Na	-0.5	*
		Tetralin	--	--	-9.3	*
		Tetralin	CO	--	-9.8	*
T376, T377	250°C	A04	H ₂	--	51.5	63.4
		A04	CO	--	77.6	79.1
		CA1	CO	--	66.3	72.1
		CA1	CO	Na	74.0	92.9
		Tetralin	--	--	45.1	56.4
		Tetralin	CO	--	74.0	86.3

- ^a 1000 psi charged.
- ^b Nominal conditions of 420°C and 1000 psi H₂.
- ^c Coal-derived anthracene oil.
- ^d None used.
- ^e Cresylic acid solvent.
- ^f Samples not available for analysis.
- ^g 0.05 g NaOH dissolved in 0.05 g H₂O

TABLE 2
SINGLE-STEP LIQUEFACTION TESTS PERFORMED IN THE MICROREACTOR SYSTEM^a

Run Number	Maximum Temperature	Solvent	% Conversion to THF Solubles
T372	398°C	Tetralin	78.7
		A04	69.8
		A04	73.5
T373	433°C	Tetralin	89.1
		Tetralin	91.4
		A04	57.3
		A04	61.9
		A04	76.4
		CA1	43.8
		CA1	47.4
		CA1	43.0

- ^a Using H₂ as the reductant.

TABLE 3
RESULTS OF PRETREATMENT SCHEMES TESTED IN THE AUTOCLAVE SYSTEM

Solvent	Reducing Gas	Additive	Run Number		% Conversion to THF Solubles	
			Pretreatment	First Stage	After Pretreatment ^a	After 1st Stage ^b
Tetralin	Ar	-- ^c	N459	N460	* ^d	78.9
Tetralin	Ar	H ₂ S	N457	N458	23.0	85.3
A04	Ar	H ₂ S	N455	N456	-10.6	80.0
A04	CO	H ₂ S	N463	N464	-9.2	83.0
CA1	CO	H ₂ S	N461	N462	1.8	70.9
A04	H ₂	--	N453	N454	-12.4	60.7

* At nominal conditions of 175°C and 1000 psi reducing gas.

^b At nominal conditions of 410°C and 1000 psi H₂.

^c None used.

^d Sample not available for analysis.

TABLE 4
PRODUCT SLATES OF AUTOCLAVE PRETREATMENT TEST
FOLLOWING PRETREATMENT ONLY^a

	Pretreatment Scheme				
	N457 Tet/Ar/H ₂ S	N455 A04/Ar/H ₂ S	N463 A04/CO/H ₂ S	N461 CA1/CO/H ₂ S	N453 A04/H ₂
<u>Gas</u>					
CO	0.00	0.00	-3.22	-0.12	0.00
H ₂	0.36	0.39	0.40	0.53	0.17
CO ₂	1.44	1.47	11.46	7.28	1.38
C1-C3	0.05	0.10	0.00	0.00	0.00
H ₂ S	-7.60	-0.93	-2.51	-4.07	0.00
<u>Liquid</u>					
H ₂ O	-0.68	1.55	-3.48	-1.73	-1.00
Distillable					
Oils	-69.16	-27.15	-20.77	-85.18	-37.21
Soluble Residue	96.85	12.97	8.29	84.05	24.34
Ash	1.77	1.01	0.66	1.05	-0.03
IOM	76.98	110.60	109.17	98.18	112.35

* Values are wt% based upon 100 g MAF coal in; positive values indicate production of a component; negative values indicate consumption.

TABLE 5
PRODUCT SLATES OF AUTOCLAVE PRETREATMENT TESTS
FOLLOWING FIRST-STAGE PROCESSING*

	<u>Pretreatment Scheme</u>				
	<u>N457</u> <u>Tet/Ar/H₂S</u>	<u>N455</u> <u>A04/Ar/H₂S</u>	<u>N463</u> <u>A04/CO/H₂S</u>	<u>N461</u> <u>CA1/CO/H₂S</u>	<u>N453</u> <u>A04/H₂</u>
<u>Gas</u>					
CO	0.71	0.50	0.37	-3.06	0.43
H ₂	-0.83	-1.99	-6.21	-1.36	-0.71
CO ₂	15.37	11.93	9.40	10.73	10.18
Cl-C3	2.32	2.17	1.49	1.71	1.45
H ₂ S	0.70	6.31	5.27	2.82	0.11
<u>Liquid</u>					
H ₂ O	4.37	8.30	0.79	8.58	-1.11
Distillable					
Oils	-4.34	102.50	12.23	76.51	23.15
Soluble					
Residue	59.70	-40.42	56.63	-29.98	27.26
Ash	-2.55	-4.05	0.06	-1.14	-0.07
IOM	24.55	14.75	19.97	29.06	39.31

* Values are wt% based upon 100 g MAF coal in; positive values indicate production of a component; negative values indicate consumption.

TABLE 6
SOLVENT RECOVERIES OF AUTOCLAVE TESTS

<u>Pretreatment Scheme</u>	<u>Run Number</u>	<u>Solvent Recovery, wt%</u>	
		<u>After Preconversion Treatment</u>	<u>After First Stage</u>
Tet/Ar*	N459	* ^b	98.74
Tet/Ar/H ₂ S	N457	77.09	138.31
A04/Ar/H ₂ S	N455	90.84	103.07
A04/CO/H ₂ S	N463	90.43	97.24
CA1/CO/H ₂ S	N461	71.88	133.41
A04/H ₂	N453	82.54	110.99

* Tet = tetralin; Ar = argon; CA1 = cresylic acid solvent.

^b Not available for analysis.

EFFECT OF ACTIVATION CONDITIONS ON DISPERSED IRON CATALYSTS IN COAL LIQUEFACTION

Cugini, A.V., Utz, B.R., Krastman, D., and Hickey, R.F.
U. S. Department of Energy, Pittsburgh Energy Technology Center
P.O. Box 10940, Pittsburgh, PA 15236

and
Balsone, V.

Gilbert Commonwealth, Inc., Library, PA 15129

INTRODUCTION

Ongoing research at PETC has focused on improved means of developing high surface area, well dispersed slurry catalyst options for direct coal liquefaction applications.⁽¹⁾ Compared to supported hydrol liquefaction catalysts now being employed, such catalysts can exhibit superior characteristics for use in a coal dissolution reactor, particularly with respect to loss of activity and contact with reactants during the early stages of coal liquefaction. If properly dispersed and activated, molybdenum is sufficiently active to be employed for coal liquefaction at low concentrations (<0.1 wt% based on coal). However, owing to the difficulty of recovering expensive transition elements such as molybdenum after use, iron has continued to be of interest as the basis of an economical and disposable catalyst for coal liquefaction.

The catalytic activity obtained by direct introduction of iron into the feed slurry in the form of readily available minerals such as oxides or sulfide (pyrite) concentrates is generally low. Such approaches are typically ineffective unless relatively high concentrations (several wt% based on coal) of iron are added.⁽²⁻⁴⁾ Among the factors usually contributing to the low activity are poor initial dispersion and low surface area of the added iron phase, and a tendency for aggregation and loss of surface area (sintering) of the catalytically active iron sulfide (pyrrhotite) phase under coal liquefaction conditions.⁽⁵⁾

A variety of methods have been employed to increase the initial dispersion of iron in coal liquefaction systems. Catalyst precursors have been introduced by physically mixing very small particles into the feed slurry, deposition from aqueous solutions, addition in oil soluble forms, and impregnation of the feed coal by water soluble compounds.⁽⁶⁻¹²⁾ Exploratory studies using such approaches have provided evidence for increased activity with reduction of iron particle size, the need for available sulfur donating species if non-sulfide precursors are used, and the inhibiting effect of coal on the agglomeration and growth of small particles of some iron catalyst precursors under liquefaction conditions. The studies also suggest that iron may be an effective liquefaction catalyst at concentrations well below 1 wt% of the feed coal by utilizing the proper precursors, introduction techniques, and activation conditions.

Based upon a review of past research and initial screening tests, an approach combining both coal impregnation and precipitation techniques to generate a highly active dispersed iron catalyst has shown considerable promise in liquefaction tests at PETC.⁽¹³⁾ In effect, the carbonaceous matrix of the coal is being used as a support not only to disperse added iron but also to help sustain the initial high dispersion achieved subsequent to activation. Effort to date has been primarily directed toward a hydrated iron oxide (FeOOH) precursor, since sub-micron oxide particles are readily formed under the proper conditions.⁽¹⁴⁾ The approach being pursued appears to be of rather general applicability in coal liquefaction, utilizes no expensive reagents, minimizes the iron requirement, and is capable of being adapted for use on a larger processing scale.

EXPERIMENTAL

Feedstocks

Experiments were conducted with -200 mesh Illinois No. 6 (Burning Star No. 2) coal obtained from the Consolidation Coal Company. Analyses of the ground coal are given in Table 1.

Second stage heavy distillate from recent operations in a close-coupled integrated two-stage liquefaction mode at the Wilsonville Advanced Coal Liquefaction Test Facility was used as the liquefaction vehicle.⁽¹⁵⁾ The bituminous coal was slurried with second stage vacuum tower overheads (V-1074) from Run 257 (Illinois No. 6 coal). Properties of the vehicle are summarized in Table 2.

Catalyst Precursors

For use in experiments testing the effect of physically mixing catalyst precursors into the feed slurry, FeOOH was prepared by precipitation from a ferric nitrate solution (200 g/L) with sufficient ammonium hydroxide to provide a three-fold excess of NH_4^+ to Fe. A sample of Fe_2O_3 , with a nominal particle size of one micron, was used as obtained from Spang and Company, Butler, PA. A pyrite concentrate was used that originated from the Robena coal preparation facility of the U.S. Steel (now USX) Corporation. All other chemicals and reagents were ACS grade.

Two molybdenum catalyst precursors were tested to establish a basis for comparison with the iron catalysts. These precursors were ammonium heptamolybdate (AHM) and ammonium tetrathiomolybdate (ATTM). The use of these precursors to form a dispersed MoS_2 catalyst at liquefaction conditions has been documented. (1,16 and 17)

FeOOH was also dispersed onto the feed coals by an incipient wetness impregnation/precipitation approach. A solution of 1 g of ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in 40 g of distilled water was used to wet 50 g of the ground bituminous coal to incipient wetness. The wet paste was added rapidly to a solution containing 20 g of ammonium hydroxide (29% NH_3) and 200 g of distilled water. Pressure-filtration of the aqueous coal suspension through a 0.45 micron filter resulted in a clear filtrate. The iron loaded coal was vacuum dried at 40°C.

X-Ray diffraction studies were conducted with a Rigaku computer-controlled diffractometer equipped with a long fine-focus Cu X-ray tube, a receiving graphite monochromator to provide monochromatic Cu-K_α radiation, and a scintillation detector.

Liquefaction Tests

Catalyst screening tests were conducted in 40-mL microreactors for 1 hour at 425°C using a 10g total charge of 2:1 vehicle (tetralin) to coal ratio. In tests comparing the effect of an added source of sulfur to ensure sulfiding of the iron, 0.1 g of CS_2 was added to the charge. Heat-up rates of 2-3 minutes were obtained by immersing the microreactor in a fluidized sand bath preheated to 425°C. Coal conversion was calculated from the solubility of the coal-derived products in methylene chloride and in heptane determined by a pressure filtration technique, based on weight of insoluble residue.⁽¹⁸⁾

Semi-batch (batch slurry, flow through gas) tests were performed in a 1-L stirred-tank reactor system to obtain more definitive product yield and conversion information and sufficient product for additional characterization. The feed charge consisted of 500 g of 30 wt% coal slurry. Reactions were run at 425°C for 1 hour under 2500 psig of $\text{H}_2/3\%\text{H}_2\text{S}$. The gas feed rate was 4 SCFH. A 100 g aliquot of the reactor product was subjected to a single-stage vacuum distillation to approximate the 650°F, 650°F-950°F, and 950°F+ content. The 650°F- fraction was separated by

distillation at a pressure of 50 torr to a vapor temperature of 462°F. The product distillation was taken to a pressure of 5 torr and vapor temperature of 610°F to approximate the 950°F+ yield. A second 100 g aliquot of the reactor product was used to determine solubility yields following the general product workup scheme outlined in Figure 1. The product gas composition was determined by on-line gas chromatography monitoring and by the analysis of gas burette samples.

Further tests were performed in a computer-controlled 1-L bench-scale continuous liquefaction unit. A schematic of the unit is shown in Figure 2. For experiments with iron, an intermediate stage was added to assist in activating the catalyst precursor. The residence time in this intermediate stage was approximately 20 minutes. Continuous operations were carried out with a 30 wt% coal slurry, reactor temperature of 435°C, 2500 psig $H_2/3\%H_2S$, and 1-h residence time. The gas flow rate was 4 SCFH; the slurry feed rate was 240 g/h. The product workup scheme in Figure 1 was followed.

Activation Studies:

The 40 mL microautoclave reactor was used to investigate the effect of activation temperature on the transition of FeOOH to pyrrhotite. In these experiments, FeOOH was impregnated onto carbon black rather than coal to eliminate the interferences caused by the indigenous pyrite in the coal. The carbon black was Raven 22 Powder obtained from Columbian Chemicals Co. The iron loaded carbon black and tetralin were rapidly heated (under H_2 in the presence of CS_2) to temperatures of 100°C, 150°C, 200°C, 250°C, 300°C, 350°C, and 400°C and held at temperature for 5 minutes. The products were mixed with THF and filtered through a 0.45-micron filter paper. The filter cake, containing the iron loaded carbon, was recovered and analyzed by X-Ray diffraction.

RESULTS AND DISCUSSION

Catalyst Screening Experiments

A series of microautoclave screening experiments was initially conducted with Illinois No. 6 coal and a variety of iron additives. Results with no added iron, several iron oxide preparations, and AHM are compared in Figure 3. Coal conversions to heptane and methylene chloride solubles were similar in the presence of 5000 ppm iron as 1-micron particles of iron oxide or in the presence of H_2S (from addition of 0.1 wt% CS_2) with no added iron. Although not shown, introduction of 5000 ppm iron in the form of powdered coal-derived pyrite or dilute solutions of ferrous sulfate, or ferrous ammonium sulfate gave results comparable to physically mixing the powdered iron oxide into the tetralin/coal charge. Tests with powdered FeOOH gave some improvement in coal conversions. These conversions were further enhanced by addition of a sulfiding agent. The highest catalytic activity was developed after dispersion of the FeOOH precursor on the coal surface by an incipient wetness impregnation/precipitation procedure. Coal conversions with 2500 ppm iron added by this procedure were comparable to those obtained by addition of 1500 ppm molybdenum as a dilute solution of AHM. The screening studies indicate that the presence of hydrogen sulfide (or another sulfur source) is required to transform the FeOOH precursor into its most active form.

The general trends in liquefaction activity of the iron oxides in Figure 3 are consistent with expectations based on particle size considerations. The initially high metal dispersion that may be attained by solution impregnation can be largely lost in the subsequent drying procedure. The PETC procedure minimizes this problem by rapidly precipitating and fixing the precursor onto the coal surface in an insoluble form before drying. It is important that the coal surfaces only be wetted to incipient wetness during the impregnation step prior to precipitation. A procedure in which the coal is suspended in the impregnating solution and then treated with base to

deposit FeOOH on the coal has been described by Mukherjee and coworkers.⁽⁸⁾ As shown in Figure 4, results obtained by this approach are only marginally better than those obtained by physically mixing the FeOOH precursor into the coal/solvent feed.

Liquefaction Tests

Semi-batch stirred autoclave tests were conducted with Illinois No. 6 coal. Conversions at 425°C to soluble and distillate products obtained with the impregnated FeOOH, AHM, and no added catalyst are compared in Figure 5. Yield structures for 2500 ppm added iron (as impregnated FeOOH) and 1500 ppm molybdenum (as aqueous AHM) are presented in Table 3. The yield structure for the two cases appears to be similar. However, for the particular liquefaction conditions and active metal concentrations chosen, a higher total distillate yield was obtained from the iron catalyst. Elemental analysis of the distillation product fractions indicated little difference between the products from using FeOOH or AHM as the catalyst precursors.

The transitions involved in the generation of pyrrhotite from impregnated FeOOH were studied in a series of microautoclave experiments. The results are given in Table 4. These results indicate that a transition from amorphous to crystalline form occurs between 300°C and 350°C, after which crystalline pyrrhotite is observed. It is likely that pyrrhotite is present at temperatures below 350°C. The pyrrhotite present below 350°C must be smaller than 100 Å, since it was not detectable by X-Ray diffraction. Consequently, it may be expected that pyrrhotite formed prior to 350°C would exhibit a higher liquefaction activity than the pyrrhotite formed at 350°C.

A continuous unit evaluation of the impregnated iron catalyst was made with Illinois No. 6 coal. Table 5 compares product yields in this test using FeOOH and an activation temperature of 275°C with those obtained in a continuous unit test using dispersed molybdenum, added as aqueous ammonium tetrathiomolybdate (ATTM), as the catalyst. Under these liquefaction conditions, the observed conversions with iron are comparable to the observed conversions with molybdenum.

The effect of varying the intermediate temperature was investigated in a series of continuous liquefaction tests. Table 6 summarizes the results. The highest levels of conversion and smoothest operation were observed at 275°C. At 350°C, coal conversions were lower than at 275°C and operation of the unit was more difficult; minor plugging problems were observed. Below an activation temperature of 275°C the FeOOH may not have been fully sulfided (converted to pyrrhotite) and, therefore, did not exhibit the same catalytic activity as the pyrrhotite formed at 275°C. The decrease in coal conversion and more difficult unit operation at the higher activation temperature suggest that the pyrrhotite formed at 350°C was catalytically less active than at 275°C. This may be due to formation of the pyrrhotite having a larger crystallite size at 350°C than at 275°C. However, the results could also be attributed to thermal soaking differences between 275°C and 350°C. However, in earlier studies with the molybdenum system⁽¹⁷⁾, it was reported that the effect of thermal soaking was not observed. It has not been established that 275°C represents the optimal intermediate temperature; 275°C is an activation temperature that results in higher coal conversions using the dispersed iron catalyst than activation temperatures that are significantly different. Further studies of the effect of the activation temperature and residence time are being made.

Owing to differences in surface properties, functionality, and liquefaction characteristics between bituminous and subbituminous coals, it cannot be assumed that the exact iron catalyst precursor dispersion and activation conditions that are optimal for a bituminous coal are directly transferable to the case of a subbituminous coal. Preliminary semi-batch studies suggest that higher concentrations of an added sulfiding agent are required to fully activate the iron catalyst on low-sulfur bituminous coals. The optimal catalyst activation temperature in continuous operations may also be different for subbituminous coals. Extension of the current iron dispersion and activation approach to a subbituminous coal is currently under investigation.

SUMMARY

A procedure for dispersing a finely divided form of iron on coal has been developed that yields a highly active catalyst for direct coal liquefaction applications. Feed coal is impregnated with Fe^{3+} by an incipient wetness procedure. Subsequently, the high dispersion and interaction with the coal surfaces is maintained by conversion of the added iron to an insoluble hydrated iron oxide (FeOOH). Proper activation of this dispersed hydrated iron oxide under typical liquefaction conditions is shown to result in an effective disposable catalyst for the conversion of coal. In batch or semi-batch operations proper activation can be achieved during heat-up of the reactants. In continuous operations, an activation reactor stage is required.

Using iron concentrations as low as 2500 ppm (based on coal), batch liquefaction tests were conducted with Illinois No. 6 coal slurried with solvents from the Wilsonville Advanced Coal Liquefaction Test Facility. Conversions of the coal to distillate and soluble products at 425°C under 2500 psig of $\text{H}_2/3\% \text{H}_2\text{S}$ for 1-h compared favorably with conversions under the same conditions using 1500 ppm of molybdenum added as ammonium heptamolybdate (AHM).

Bench-scale continuous-unit tests to better define the activation sequence of the iron catalyst in continuous operations were conducted with Illinois No. 6 coal. At an activation temperature of 275°C (and activation residence time of 0.33 hour) and a final reactor temperature of 435°C and residence time of 1 hour, the conversions observed with the impregnated FeOOH catalyst precursor were again similar to the conversions observed using added Mo. Significantly varying the activation temperature from 275°C results in poorer liquid yields and unit performance. Below 275°C sulfiding of the FeOOH precursor may be a problem; above 275°C the growth of pyrrhotite crystals may be detrimental to the liquefaction activity of the iron.

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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Table 1. Analyses of Illinois No. 6 (Burning Star).

Proximate Analysis, (As Received)		wt%
Moisture		4.2
Volatile Matter		36.9
Fixed Carbon		48.2
Ash		10.7
Ultimate Analyses, (Moisture Free)		wt%
Carbon		70.2
Hydrogen		4.8
Nitrogen		0.9
Sulfur		3.1
Oxygen (Difference)		9.9
Ash		11.1
Sulfur Forms		wt%
Sulfatic		0.03
Pyritic		1.2
Organic		1.9

Table 2. Properties of V-1074 oil.

<u>Ultimate Analysis</u>	<u>wt%</u>
Carbon	89.1
Hydrogen	9.8
Oxygen (Direct)	0.9
Nitrogen	0.4
Sulfur	0.04
Ash	<0.1
850°F (Vol%)	65
Heptane Insols, wt%	0.2
M _n (daltons)	360 ^a
H ⁺ _{ar}	0.15
f _a	0.43

^aVPO, tetrahydrofuran, 40°C

Table 3. Product yields from liquefaction of 30 wt% Illinois No. 6 coal and 70 wt% V-1074 in a semi-batch mode non-catalytically, with added iron (FeOOH) and added molybdenum (AHM). (Semi-batch 1-L autoclave; Reactor Temp. = 425°C, Time at Temperature = 1 hour, Pressure = 2500 psig, 97%H₂/3%H₂S; Fe conc. = 2500 ppm, Mo. conc. = 1500 ppm, Gas Feed Rate = 4 SCFH.)

Yield Structure (Ash Free Basis), Wt%

<u>Component</u>	<u>Non-Catalytic</u>	<u>FeOOH</u>	<u>AHM</u>
C ₁ -C ₄	3.2	3.0	2.3
C ₅ -950°F	71.8	82.9	81.5
950°F+ Solubles	10.0	6.2	8.6
Heptane Insolubles	15.3	8.3	8.6
Non-Hydrocarbon Gases	1.0	1.0	1.0
Hydrogen	(1.3)	(1.6)	(2.0)

Table 4. Microautoclave Iron Activation Studies Using Carbon Black and Tetralin 1000 psig H₂ Cold Pressure with Added CS₂ Using 2500 ppm Iron as Hydrated Iron Oxide on Carbon

<u>Final Reactor Temperature °C</u>	<u>Dominant Iron Phase by X-Ray Diffraction</u>	<u>Pyrrhotite Area Under Curve</u>	<u>Estimated Crystallite Size</u>
100	Amorphous		
150	Amorphous		
200	Amorphous		
250	Amorphous		
300	Amorphous		
350	Pyrrhotite	87	400Å
400	Pyrrhotite	158	400Å

Table 5. Product yields from liquefaction of 30 wt% Illinois No. 6 coal and 70 wt% V-1074 in a continuous mode with added iron (FeOOH) and added molybdenum (ATM). (Continuous 1-L autoclave; Reactor Temp. = 435°C, Pressure = 2500 psig, 97% H_2 /3% H_2S ; Fe conc. = 2500 ppm, Mo conc. = 1000 ppm, Gas Feed Rate = 4 SCFH; Slurry Feed Rate = 240 g/h.

Yield Structure (Ash Free Basis), Wt%

<u>Component</u>	<u>FeOOH</u>	<u>ATM</u>
C ₁ -C ₄	3.4	3.2
C ₅ -950°F	82.7	83.5
950°F ⁺	15.0	14.5
Non-Hydrocarbon Gases	1.4	1.4
Hydrogen	(2.5)	(2.6)

Table 6. Continuous Unit Iron Activation Studies Using Illinois No. 6 Coal and Wilsonville Recycle Solvent (30 wt% Coal in Solvent), 2500 psig (3% H_2S in H_2) Using 2500 ppm Iron as Hydrated Iron Oxide on Coal

Total Product

<u>Reactor #1 Temp. °C</u>	<u>Reactor #2 Temp. °C</u>	<u>% 950°F+ in Total Product</u>	<u>% Methylene Chloride Insolubles</u>	<u>% Heptane Insolubles</u>	<u>Comments</u>
150	435	***	***	***	Plugged - after 12 hours
275	435	15	7.6	14.2	Smooth Operation - 32 hours
350	435	22	12.4	20.6	Rough Operation - 32 hours
50	435	***	***	***	Plugged - after 2 hours
275	435	16	6.4	13.0	Smooth Operation - 72 hours Normal Shutdown

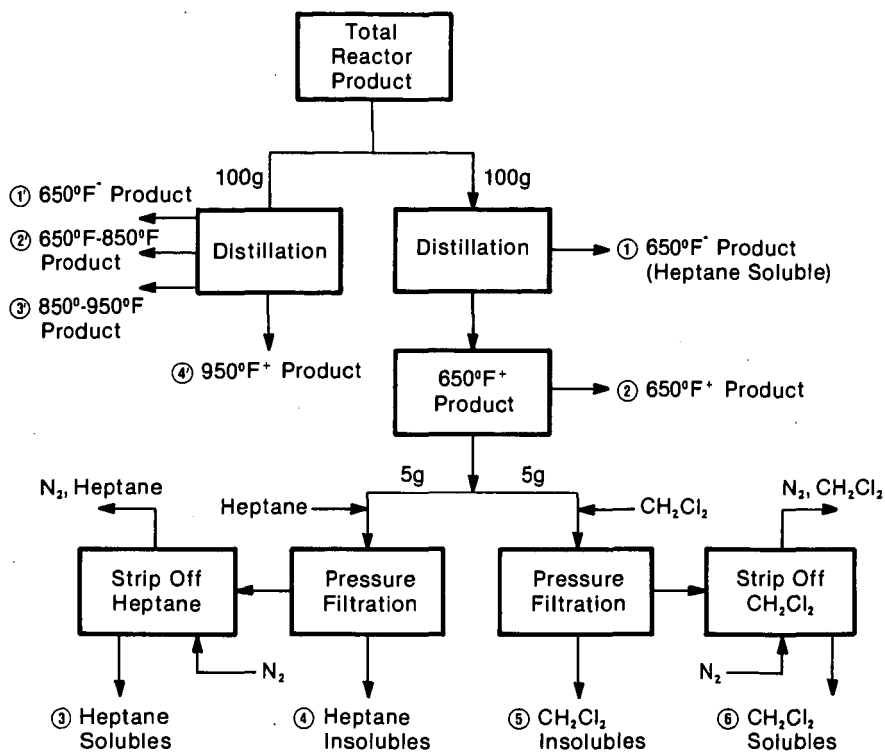


FIGURE 1. PRODUCT WORKUP SCHEME FOR 1-LITER SEMI-BATCH AND CONTINUOUS UNIT OPERATIONS.

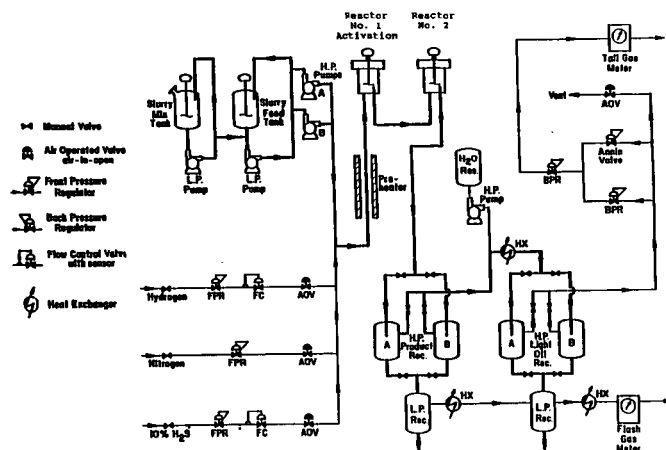


Figure 2. Bench-scale continuous unit configuration.

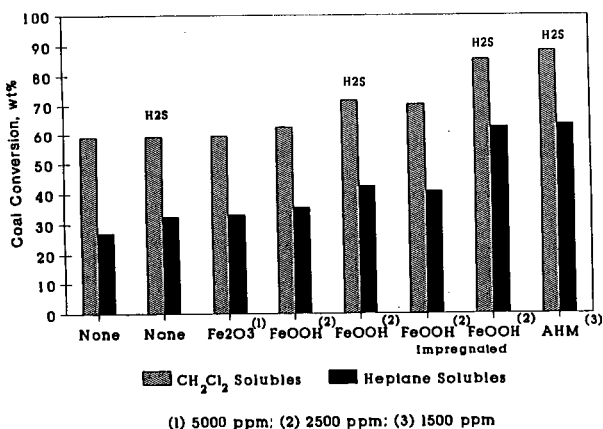
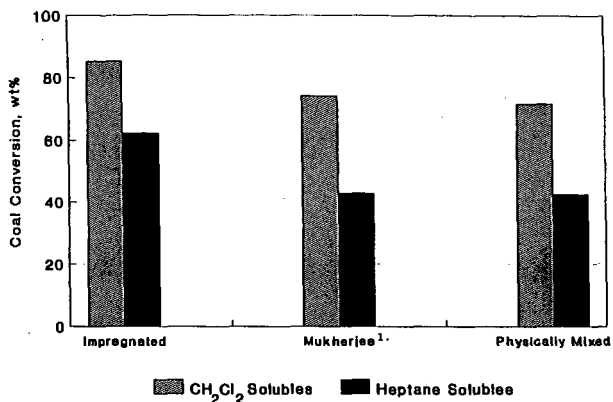
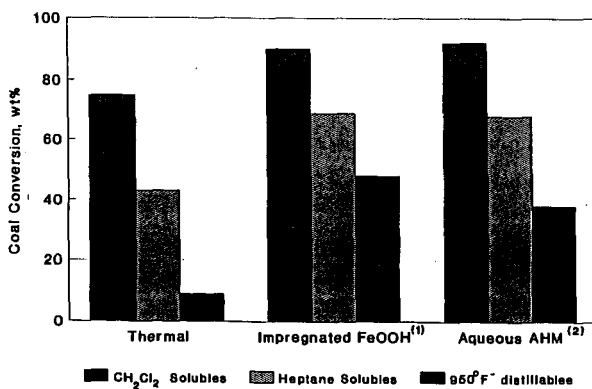


Figure 3. Effect of catalysts on coal conversion. (Microautoclave runs; 425°C, 1h, 2500 psig H₂, 2:1 tetralin:Illinois No. 6 coal)



1. Coal/Catalyst mixture prepared according to procedure outlined in reference 8.

Figure 4. Effect of impregnation on coal conversion. (Microautoclave runs; 425°C, 1h, 2500 psig H₂, 0.1 g CS₂, 2:1 tetralin:Illinois No. 6 coal)



(1) 2500 ppm; (2) 1500 ppm

Figure 5. Effect of catalysts on coal conversion. (1-L semi-batch experiments; 425°C, 1h, 2500 psig, 97% H₂/3% H₂S at 4 SCFH)

DESIGNED COAL LIQUEFACTION CATALYSTS

A. S. Hirschon and R. B. Wilson Jr.

SRI International
Inorganic and Organometallic Chemistry Program
Menlo Park, California 94025

Keywords: coal liquefaction; catalysts; preconversion

ABSTRACT

The effects and ramifications of using highly dispersed catalysts for coal liquefaction are discussed. We have briefly explored several types of iron and molybdenum based complexes as precursors to high dispersion catalysts. The precursors were either organometallic complexes or water soluble salts and were impregnated into coals of various ranks. The molybdenum catalysts were found to be very effective for an Illinois #6 bituminous coal whereas the iron catalysts were not. In contrast, the iron catalysts were found to be very effective for lignite conversions. Both a H-donor conversion system and a non-donor system were compared, using tetralin and n-hexadecane, respectively. In each case the organometallic precursor gave greater yields of toluene soluble material, with differences being most dramatic in the hexadecane system. The yields using the organometallic molybdenum precursors in hexadecane were found to be almost as great as those in the tetralin system, indicating that with a good enough catalyst precursor, donor solvents are not needed.

INTRODUCTION

One of the keys to a successful coal liquefaction process is the control of preconversion reactions. Coal is composed of numerous functional groups and classes of molecules. Depending on reaction conditions, these groups may either undergo polymerization and char formation, or bond breaking reactions to form gases and coal liquids. These reactions may occur at quite low temperatures, and thus finding appropriate process conditions and reactive catalysts to control these reactions is critical. For instance, several workers have shown that phenolics tend to polymerize into difficult to upgrade materials unless treated by some means such as a donor solvent such as tetralin (1,2). Current liquefaction processes have shown the benefits of staging the severity of the liquefaction process in order to control preconversion reactions, but are limited in choices of catalyst. Supported catalysts are often used for these processes but suffer in that they only interact with the liquefaction solvent, and have very poor intimate contact with the individual coal molecules. The function of these supported catalysts is primarily to transfer hydrogen to the liquefaction solvent. A more efficient process would involve highly dispersed catalysts that have intimate contact with the coal molecules, have high surface areas or are soluble so that only small amounts of catalyst are needed, and most importantly, would be active at preconversion conditions to limit the amount of retrogressive reactions that occur in the initial stages of coal liquefaction.

Generally, efforts to use dispersed catalysts during coal liquefaction utilize precursors that are not activated until high temperatures (3-6). For instance, molybdenum is often added as either the oxide, the thiolate water soluble salt, or as molybdenum naphthenate, so the molybdenum must first be transformed from the oxide to the trisulfide, and finally transformed to the disulfide, the most active form of the catalyst. However, the conversion of the trisulfide to disulfide occurs only under high temperatures, in excess of 350°C (7). Likewise, a commonly used iron precursor, iron oxide, is difficult to convert to the active pyrrhotite and requires high temperature activation. A soluble organometallic precursor, iron carbonyl has also been investigated; however, it likewise is difficult to activate and tends to form iron carbides and oxides during the activation process (6).

In recent work we have investigated precursors designed to have the correct stoichiometry of the active catalyst (8-10). These precursors can form high surface area catalysts that are active at low temperatures, and thus may limit the polymerization or retrogressive reactions that occur during coal preconversion. The following work describes our efforts to study the reactivities and effects of these types of catalysts for coal liquefaction. Our goals are to synthesize and test soluble complexes that are as close to the correct stoichiometry and structure of the active catalyst during the coal liquefaction. Thus we hope that our catalysts, since they do not require high temperature activation, will cause bond breaking reactions at lower temperatures than are currently possible with dispersed catalysts, and may therefore aid in reducing retrogressive reactions.

EXPERIMENTAL

The coals used were PSOC 1098 Illinois #6 and Beulah-Zap North Dakota lignite from the Argonne coal bank. The ratio of catalyst to coal was approximately 0.6 mmoles of metal per gram of coal. The organometallic molybdenum catalyst was $\text{Cp}_2\text{Mo}_2(\mu\text{-SH})_2(\mu\text{-S})_2$, referred to as $\text{MoS}_2(\text{OM})$, and was prepared by modification of method of Dubois et al. (11). Pentacarbonyl iron was obtained from Aldrich, and the sulfur-containing iron cluster, $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ was prepared by the method of Bogan et al. (12). Ammonium tetrathiomolybdate, $\text{MoS}_4(\text{Aq})$, was obtained from Alfa Chemicals. The organometallic catalysts were impregnated into the coal in tetrahydrofuran (THF) with the exception of the iron complexes, where the reaction solvent was used. The THF was removed by evaporation under vacuum at room temperature. The molybdenum salt was added as an aqueous solution. The coal liquefaction experiments were conducted in a 300 mL Autoclave Engineers stirred reactor using 5.0 g of coal, 30 g of liquefaction solvent, and 500 psig hydrogen. Temperatures of either 400°C or 425°C for 20 minutes using either tetralin or n-hexadecane were used for these conversions. After the reaction had cooled, the coal liquid and residue were taken up in THF. The THF was removed under reduced pressure and the residue taken up in toluene. The product was filtered through a medium porosity filter and separated into toluene soluble (TS) and insoluble (TI) fractions. The toluene and residual tetralin, if used, were then removed from the TS under reduced pressure. The TS and TI fractions were then dried at 76°C for 12 h under vacuum (< 0.1 mm). The conversions were calculated from the amount of toluene-insoluble material and are based on daf basis, or the carbon balance, as in the case of the lignite.

RESULTS AND DISCUSSION

Data from coal conversions in tetralin and hexadecane solvent systems are presented in Tables 1 and 2, respectively. The Illinois #6 coal gave quite high conversions to toluene soluble material even under the mild conditions of 500 psig hydrogen pressures and 400°C when tetralin was used for the coal liquefaction, as expected for a high volatile bituminous coal. Also as expected, it gave poor conversions in the absence of catalyst in the non-donor hexadecane solvent. The tetralin appeared to moderate the effects of the catalysts, so that the range of conversions was only about 13%. For example, the conversion to toluene soluble material in the absence of catalyst in tetralin was 48%,

compared to 53% when impregnated with aqueous molybdenum, and 61% the coal was impregnated with organometallic molybdenum. A similar range was observed with the conversion temperature increased to 425°C. The iron catalyzed reactions, utilizing $\text{Fe}(\text{CO})_5$ and the iron sulfido dimer, $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$, designated as Fe_2S_2 showed no apparent effect from the non-catalyzed conversions. However, the TS product of the Fe_2S_2 catalyst was a tar while the product from the $\text{Fe}(\text{CO})_5$ catalyzed reaction was a brittle solid. Experiments with model compounds have shown that the $\text{Fe}(\text{CO})_5$ tends to form tars as well as metal carbides and oxides, whereas the $[\text{SFe}(\text{CO})_3]_2$ shows no evidence of polymerization reactions or other products besides iron sulfides, and we suggest that further investigation of these products will show that the latter gives a better quality product.

The oxygen content of the TS product of the catalyzed conversions were found to be lower than those of the non-catalyzed runs. For instance, the molybdenum catalyzed reactions had the lowest oxygen content of 4.6 to 4.8% oxygen, the iron catalyzed reactions gave a 5% oxygen content, and the base line runs an oxygen content of 6-6.5%. The lower oxygen content is one of the goals of our work, since many of the retrogressive reactions are thought to center through this group. In future work we hope to determine whether the reduction of oxygen occurs during the preconversion reactions as we speculate, or during the more severe reactions during coal conversion.

Table 2 lists conversions in hexadecane. The use of hexadecane rather than a typical conversion medium was induced by the desire to use a non-reacting, non-donor conversion medium that would not interfere with the study of the catalysts. As shown in the table, most of the conversions are quite low, as expected. For instance in the absence of catalyst the Illinois #6 coal was converted to 25% toluene soluble material, compared to 48% in tetralin. However, in the presence of the molybdenum catalysts, the conversions were greatly enhanced. For instance, the aqueous molybdenum impregnation gave a conversion of 41% and the organometallic molybdenum impregnation resulted in a conversion of 54%, which is nearly as great as when tetralin was used as the conversion medium. The iron catalyzed conversions showed little effect from the non-catalyzed runs for the Illinois #6 coal; however, showed a significant improvement for the conversion of lignite, with conversions of approximately 40% toluene soluble compared to 24% with no catalyst. Thus the iron complexes appear to be best suited towards low rank coals, presumably due to their increased oxygen functionalities. The Fe_2S_2 catalyst appears to have slightly more asphaltenes in the product distribution, but future work will be needed to further study any differences in reactivities between these catalysts.

CONCLUSIONS

Dispersed catalytic liquefaction has several distinct advantages over conventional thermal or catalytic liquefaction. In the presence of hydrogen, a suitably dispersed catalyst can provide a highly reducing environment within the coal matrix, thus eliminating the need for a good hydrogen donating solvent. An added advantage to these catalysts is that they can promote certain bond cleavage reactions during the liquefaction step. If they can aid in removing the heteroatoms, namely oxygen and nitrogen, during the early stages in coal liquefaction, then the detrimental retrogressive reactions would be minimized. Thus a better quality coal liquid product would be produced that would be easier and less expensive to hydrotreat. The high activity of the molybdenum sulfido complex, we believe, is because the catalyst was impregnated in a highly active form, and thus does not require subsequent activation during the liquefaction step, and thus is active during the preconversion reactions preventing retrogressive reactions. The organometallic iron complexes were found to be effective for low rank coals, and in future work we hope to understand their role in liquefaction in order to better design a more effective liquefaction catalyst.

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Table 1
Conversion to Toluene Soluble Products in Tetralin^a

Catalyst	T (°C)	% TS	% O
None	400	48	6.0
MoS ₄ (Aq)	400	53	4.8
MoS ₂ (OM) ^b	400	61	4.6
Fe(CO) ₅	400	47	5.0
Fe ₂ S ₂	400	49	5.1
None	425	69	4.0
MoS ₂ (OM) ^b	425	84	2.3
MoS ₄ (Aq)	425	76	4.0

^aReaction conducted in 300-mL autoclave with 5 g Illinois #6 coal in 30 g solvent and 500 psi H₂ at for 20 min.

^bOM refers to organometallic precursor.

Table 2
Conversion to Toluene Soluble Products in Hexadecane^a

Catalyst	Coal	T (°C)	% TS
None	Ill. # 6	400	25
Fe(CO) ₅	Ill. # 6	400	24
Fe ₂ S ₂	Ill. # 6	400	29
MoS ₄ (Aq)	Ill. # 6	400	41
MoS ₂ (OM)	Ill. # 6	400	54
None	Lignite	425	24
Fe(CO) ₅	Lignite	425	41
Fe ₂ S ₂	Lignite	425	39

^aReaction conducted in 300-mL autoclave with 5 g coal in 30 g solvent and 500 psi H₂ at for 20 min.

^bOM refers to organometallic precursor.

DRYING OF BEULAH ZAP LIGNITE

Karl S. Vorres*, Donald Molenda* and

Yuhong Dang**, Vivak M. Malhotra**

*Chemistry Division, Building 211

Argonne National Laboratory

Argonne, IL 60439

**Physics Department

Southern Illinois University at Carbondale

Carbondale, IL 62901-4401

Keywords: drying, liquefaction, differential scanning calorimetry (DSC), FTIR, TGA

INTRODUCTION

The drying of low rank coal is important in effective liquefaction of this abundant resource. It has been said by several researchers that a small reduction of moisture in these coals does not adversely affect the liquefaction behavior, however a very large amount of drying does have an adverse effect on the rates of this reaction. It has been felt that this behavior may be due to the possible irreversible change in physical pore structure that was believed to accompany drying.

It is generally recognized that the physical structure of coal is composed of three components: an organic matrix, inorganic matter, and an extensive network of pores. It is also believed that the pore network usually contains water in 'as-mined' coals. Mraw and Silbernagel (1) suggested that the amount of water present in as-mined coals provides a measure of pore volume. However, Kaji et al. (2) examined the water-holding capacity, specific surface area, and pore volume of 13 coals from various locations, ranging from lignite to anthracite, and found no correlation between the water-holding capacity and the pore volume. Based on the assumption that the total coal oxygen is distributed uniformly through the coal and the functional-group oxygen increases with oxygen content, Kaji et al. found a linear relationship between the hydrophilic sites and the water-holding capacity of coal. It seems to us that the relationship between the total oxygen content of coal and the water-holding capacity is more fortuitous than real since oxygen-functional groups are not the only hydrophilic sites in coal (3). Moreover, the presence of minerals, especially smectite lattices, and various cations will also strongly influence the coal-water interactions.

Vorres et al. (4) and Vorres and Kolman (5) adopted the approach of ascertaining the kinetics of vacuum drying of coal as a means to understand the complex coal-water interactions. From isothermal thermogravimetry analysis, i.e., the weight loss vs. time at fixed temperature, Vorres and his co-workers indicated that the dehydration of Illinois No. 6 in the form of a block, -20 mesh, and -100 mesh, follows a desorption kinetics mechanism. Thus, they concluded that the rate controlling mechanism of dehydration is governed by the surface of coal. In addition, Vorres and his co-workers indicated that the particle size and the history of coal also affect the dehydration kinetics of coal. More recently, Abhari and Isaacs (6) used the thermogravimetric

analysis (TGA) technique to explore the drying kinetics of six coals from the Argonne coal-sample bank. They evoked a bulk moisture/pore moisture model to explain the observed drying kinetics for the six coals, in which the order of kinetics, i.e., the order of dehydration showed a strong dependence on the rank of coal. In calculating the kinetics parameters from the weight loss data, these researchers assumed that water in coal is held by the physisorption process. This assumption is at variance with the temperature dependent NMR results (7) and the contention of Kaji et al. (2).

In this paper, we report our recent results on the kinetics of water's desorption from Beulah-Zap lignite coal, as determined by thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC) technique. The kinetic analysis of DSC was further complimented by determining the mechanism of air drying of lignite coal with the help of an in-situ Desorption Kinetics via Fourier transform infrared (ISDK-FTIR) technique.

EXPERIMENTAL

Isothermal Thermogravimetry

Coal drying was done with a Cahn model 121 thermobalance attached to an IBM PC/XT microcomputer. Vendor-supplied software was used to monitor the progress of individual runs, and convert data files to a form that could be further studied with Lotus 123.

The data were obtained as files of weight at 10 second intervals. For runs longer than 10 hours, the runs were modified to work with data points at 20 second intervals.

The typical sample size was about 140 mg. The sample was placed in a platinum hemispherically-shaped pan. Sample sizes included the two mesh sizes of the usual Argonne Premium Coal Samples (-100 and -20 < 84 μ) and also one or two small pieces which came from lumps which have been stored under nitrogen since the time of the acquisition of the original samples. A sample of -400 mesh (< 37 μ) material was prepared at Southern Illinois University at Carbondale with a Brinkmann Micro-Rapid mill.

Data were analyzed by testing the weight loss as a function of time with 13 different kinetic expressions including geometrical, unimolecular, first and second order diffusion to establish a best fit. Lotus 123 was used for analysis of individual run data.

Samples were quickly transferred from freshly opened ampoules or bottles which had been kept in constant humidity chambers with water at room temperature (293°K). In the thermobalance system a period of 5 minutes was used to stabilize the system and initiate data acquisition. Room temperature runs were made with and without the furnace in place. The furnace was used for runs at 313 and 353°K. A typical run is shown in Figure 6.

For comparison, a run was made at room temperature under vacuum with the -20 mesh material.

The gas atmosphere was cylinder nitrogen (99.99%) used without further purification and passed over the sample at a rate of about 100 cc/min.

Differential Scanning Calorimetry (DSC) Measurements

The kinetics of water's desorption from lignite coal was evaluated using a non-isothermal approach in which the coal sample temperature was progressively raised at a constant heating rate (8-10). Janikowski and Stenberg (11) and Elder and Harris (12) from their DSC measurements have shown that when coal samples are subjected to thermal treatment a broad endothermic peak is observed at around 323 K - 423 K. This broad peak has been associated with the water loss from the coal. Therefore, a careful DSC experiment at $300\text{ K} < T < 473\text{ K}$ under inert environment can provide information on the kinetics of water's desorption from coal. We chose -20 mesh and -400 mesh particle size coal to explore the kinetics of water's desorption from coal. The as-received sample of Beulah-Zap lignite coal was of -20 mesh size, and the sample was received in a sealed ampule. A part of the -20 mesh coal sample was ground in a Brinkmann Micro-Rapid mill to reduce its particle size to -400 mesh. The ground sample was sieved through a -400 mesh sieve, and the -400 mesh particles were collected for DSC measurements.

The desorption of water from -20 mesh and -400 mesh particle size lignite coal was determined with the help of a well calibrated (13,14) Perkin-Elmer DSC7 system. Prior to recording the DSC curves, the lignite coal samples were kept at a 93% relative humidity (RH) for 48 hours in a humidity controlled chamber. Afterwards, about 20 mg of the samples were accurately weighed on a microbalance. The samples were then loaded in Al pans and sealed with the help of Al lids. A number of holes were drilled in the Al lids to ensure the easy escape of water vapors from the Al pans. In loading the coal samples in the Al pans, extreme care was exercised so that mechanical compacting of the particles did not control the overall desorption kinetics of water. The DSC curves were recorded at a heating rate of 10 K/min. under the controlled He purge. After the DSC runs, the sample pans were again weighed to ascertain weight loss due to the thermal treatment.

In-situ Desorption Kinetics via Transmission-FTIR (ISDK-FTIR) Measurements

The air drying kinetics of Beulah-Zap lignite coal was determined using the ISDK-FTIR technique (15). In this approach, a thin film of coal (particle size -400 mesh) was painted onto a laser grade ZnSe optical flat. The thin film was equilibrated at 93% RH in a humidity controlled chamber for 48 hours at room temperature. The desorption kinetics of water from coal was determined by mounting the coal sample in the FTIR spectrometer's sample chamber. The sample chamber was purged with a controlled flow of dry air in order to maintain a constant humidity of 9% RH. The FTIR spectra of coal were recorded as a function of time in the transmission mode. The spectra were collected by employing a fast scanning (25 scans/sec) Nicolet 740 FTIR spectrometer with a fast response liquid nitrogen cooled MCT detector. One hundred interferograms were collected at 4 cm^{-1} resolution to produce the

coal sample's FTIR spectrum. To monitor the desorption kinetics of water, a Nicolet 620 computer, interfaced with the spectrometer, was programmed to collect 100 interferograms after an interval of every 48 seconds. After the collection of 20 spectra, the time interval was increased to 80 seconds for the next 20 spectra and then subsequently to a time interval of 180 seconds. The collected interferograms were stored on a hard disk and after the completion of the experiment, the interferograms were Fourier transformed and co-added to produce the desired FTIR spectrum.

RESULTS AND DISCUSSION

Isothermal Thermogravimetry

The data were normalized to one gram of starting sample weight. The best fit of the data were obtained with a unimolecular decay kinetic expression. Plots of \ln (water left) versus time gave a characteristic shape. The plot indicates a consistent slope for about 85% of the moisture loss of the coal. A transition then occurs. The rate is then reduced to about half of the earlier rate. The kinetic parameters are given in Table 1. Values of R squared in the regression coefficient from Lotus 123 were greater than .99 for all but two of the runs. Rate coefficients, k , were obtained from the rate of change of the \ln (water left) in mg water/gram of original sample as a function of time in seconds. For a number of runs, the data did not initially fit the straight line. For these, the data included in the determination of the rate constant did not start at zero. The range of time included for the determination is indicated in the table. In the cases of initial lack of fit the rates were always above the line, indicating a more rapid moisture loss.

In general the highest R squared values are associated with the data obtained from the blocks, indicating a greater consistency with data from a singular piece of material.

The use of vacuum to remove moisture is seen to be capable of much more rapid removal of water than a stream of dry nitrogen. The ratio of the rate coefficients is an order of magnitude greater, and would imply an rate advantage to this technique for engineering for rapid processing of pulverized fuel.

The initial removal of about 85% of the moisture and then a transition to a slower rate of water loss implies a structural rearrangement. It is believed that the pores of the particles are changed after this amount of water is lost in a manner that makes the further loss of water more difficult.

DSC Results

Figure 1 reproduces the DSC curves obtained at a heating rate of 10 K min^{-1} for -20 mesh and -400 mesh particle size Beulah-Zap lignite coal. As pointed out earlier, Janikowski and Stenberg (11) observed similar endothermic broad peaks in their DSC curves at $323 \text{ K} < T < 423 \text{ K}$ from various lignite and subbituminous coal samples. At $323 \text{ K} < T < 473 \text{ K}$, water is expected to be desorbed

from the coal sample. It is worthwhile to point out here that vacuum dried samples of Beulah-Zap lignite coal showed no exothermic peaks at $323 \text{ K} < T < 473 \text{ K}$. Therefore, consistent with the observations of Janikowski and Stenberg, we also believe that the broad peak at around 373 K , as seen in Fig. 1, is produced due to the water loss from coal.

The general kinetic expression for the decomposition of a solid is

$$\frac{da}{dt} = A \exp(-E/RT) f(a). \quad (1)$$

In Eq. 1, a is the fractional conversion at a time t , k is the rate of reaction, E is the activation energy in J/mol , R is the gas constant in J/mol.K , A is the frequency factor, and T is the temperature in K . Since our DSC measurements were conducted in a non-isothermal mode, Eq. 1 was modified to take into account the constant heating rates used, i.e.,

$$\frac{da}{dT} \frac{dT}{dt} = A \exp(-E/RT) f(a). \quad (2)$$

Substituting B for the constant heating rate dT/dt used, Eq. 2 can be rewritten as

$$\frac{da}{dT} = \frac{A}{B} \exp(-E/RT) f(a). \quad (3)$$

Rearranging and integrating Eq. 3, we obtain

$$F(a) = \frac{ART^2}{BE} \left(1 - \frac{2RT}{E} \right) \exp(-E/RT). \quad (4)$$

and

$$F(a) = \int_0^a \frac{da}{f(a)} \quad (5)$$

Eq. 4 can be further simplified by taking logs, i.e.,

$$\ln \left(\frac{F(a)}{T^2} \right) = \ln \frac{AR}{BE} \left(1 - \frac{2RT}{E} \right) - \frac{E}{RT} \quad (6)$$

The fraction of the sample reacted, i.e., was determined by measuring the ratio of the partial area at temperature T to the total peak area of the appropriate DSC curves shown in Fig. 1. The isothermal kinetic expressions, given in Refs. 16 and 17, representing various decomposition models were converted into non-isothermal kinetic expressions to determine the desired $F(a)$ functions. The experimental data was then fitted to 12 non-isothermal kinetic models depicting geometrical models, the Unimolecular model, sigmoid rate models, diffusion models, and the 2nd order-diffusion model. A least squares procedure, in conjunction with Eqs. 4, 5, and 6, was adopted to ascertain the kinetics mechanism of water's desorption from lignite coal. Our calculations suggest that the Unimolecular kinetic model and 2nd-order diffusion kinetic model are simultaneously operative for the desorption of water from -20 mesh Beulah-Zap lignite coal; while for -400 mesh particle size coal, only the 2nd-order diffusion mechanism is effective. The activation energy barriers for Unimolecular decay and 2nd-order diffusion models were determined from Eq. 6. For -20 mesh particle size lignite coal the activation energies associated with Unimolecular decay model and 2nd-order diffusion model were 54 KJ/mol (12.94 Kcal/mol) and 78.5

KJ/mol (13.3 Kcal/mol), respectively. The activation energy of the 2nd-order diffusion model for - 400 mesh particle size Beulah-Zap lignite coal was 88.2 KJ/mol (21.1 Kcal/mol). The individual contributions of these kinetic models to the overall desorption of water from lignite coal were determined by fitting the experimental data to the temperature dependence of $\alpha(T)$, i.e.,

$$\alpha(T) = C_1(1 - \exp(-Y(T))) + C_2\left(1 - \frac{1}{Y(T)+1}\right). \quad (7)$$

where, $C_1 + C_2 = 1$, and

$$Y(T) = \frac{ART^2}{BE} \left(1 - \frac{2RT}{E}\right) \exp(-E/RT).$$

In Eq. 7, the first term on the right hand side represents the Unimolecular decay kinetics, while the second term depicts the 2nd-order diffusion kinetics. C_1 and C_2 for -20 mesh particle size coal were 0.23 and 0.77, respectively, while for -400 mesh particle size $C_1 = 0$ and $C_2 = 1$. Figure 2 compares the experimentally observed $\alpha(T)$ with the calculated values for -20 mesh and -400 mesh particle size Beulah-Zap lignite coal. As can be seen from Fig. 2, the agreement between the calculated values and the experimentally observed values is excellent.

The Unimolecular decay kinetics of decomposition of a solid represents a system in which each molecule has an equal probability of undergoing decomposition. In a complex system like lignite coal, the bulk type water, present as a film around the particle or present as pore water in large pores, is expected to display evaporation like characteristics. This should be especially true for water which is away from the surface of coal or is around or near the mouth of large pores. Consequently, it is argued that the observed Unimolecular decay kinetics for -20 mesh particle size coal represents the loss of bulk type water from the Beulah-Zap lignite coal. The 2nd-order diffusion kinetics represents a recombination process in which product molecules are produced with excess energy. The excess energy is then utilized in re-energizing the reactant molecules. It seems to us the water molecules hydrogen bonded to the oxygen functional groups in narrow pores and surface water in large pores will desorb via the 2nd-order diffusion mechanism. As the particle size of coal is reduced to - 400 mesh from -20 mesh, the large pores concentration in coal sample is expected to decrease. Therefore, the observation of desorption of water from - 400 mesh particle size coal via 2nd-order diffusion mechanism is not unreasonable.

ISDK-FTIR Results

Figures 3 and 4 show the observed desorption kinetics of water at $T = 294$ K from the - 400 mesh particle size Beulah-Zap lignite coal in the water's stretching and bending regions, respectively. The desorption results can be summarized as follows: (1) Three broad vibrations were observed in the O-H stretching region at 3614, 3373, and 3222 cm^{-1} as reflected by the FTIR difference spectrum at t min., i.e., FTIR spectrum at 0 min. - FTIR spectrum at t min. In the water's bending region, positive bands at 1628, 1552, 1458, and 1384 cm^{-1} and a negative band at 1740 cm^{-1} were

found in the difference spectrum. The observed desorption kinetics for the water's stretching and bending modes are shown in Fig. 5. Attempts were made to determine the desorption kinetic mechanism(s) for 3614, 3373, 3222, and 1628 cm^{-1} bands by subjecting the intensity loss data to 12 desorption kinetics models as described in Refs. 15, 16, and 17. All the water bands, be they stretch modes or bend modes, displayed a 2nd-order diffusion mechanism. Therefore, our ISDK-FTIR results support and are consistent with our conclusion from DSC measurements that water from small particles of lignite coal desorbs via a 2nd-order diffusion mechanism.

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Table 1.

Kinetic Coefficients for Beulah-Zap Lignite
(k values are in units of 10^{-5} mg water/gm original sample sec^{-1})

Data at 293°K

Run#	Mesh	k	duration (sec)	R squared
2	-100	9.0	9,000-20,000	.99993
4	-100	10.	0-19,000	.9996
14	-20	10.	0-20,000	.9998
18	Block	11.	0-	.998
22	-20	7.0	2,000-8,000	.97
23	-100	7.0	5,000-23,000	.9998
24	Block	10.	0-6,000	.99997
25	-400	11.	5,000-8,000	.9992
26	-400	11.	0-8,000	.9993
27	Block	8.0	0-12,000	.999991

Data at 313°K

Run#	Mesh	k	duration (sec)	R squared
3	-100	24.	1,000-7,000	.998
6	-100	14.	2,000-8,000	.97
11	-20	24.	3,000-9,000	.998
16	Block	23.	2,500-5,500	.9990
19	Block	19.	1,000-9,000	.9995

Data at 353°K

Run#	Mesh	k	duration (sec)	R squared
5	-100	99.	700-2,700	.997
7	-100	127	700-2,100	.9990
10	-20	131	900-2,100	.997
15	Block	85	1,100-2,900	.9994

Run in vacuum at 293°K

Run#	Mesh	k	duration (sec)	R squared
V6	-20	108.	1,000-3,000	.997

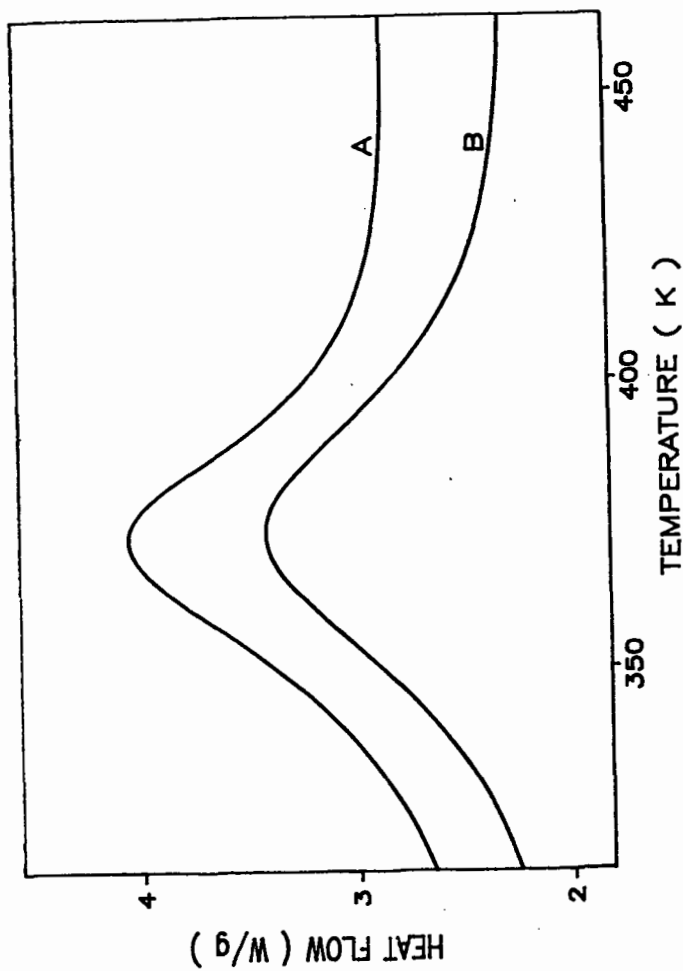


Fig. 1 The DSC curve shows the endothermic peak due to the desorption of water from Beulah-Zap lignite coal. (A) < 841 particle size, (B) < 37 particle size.

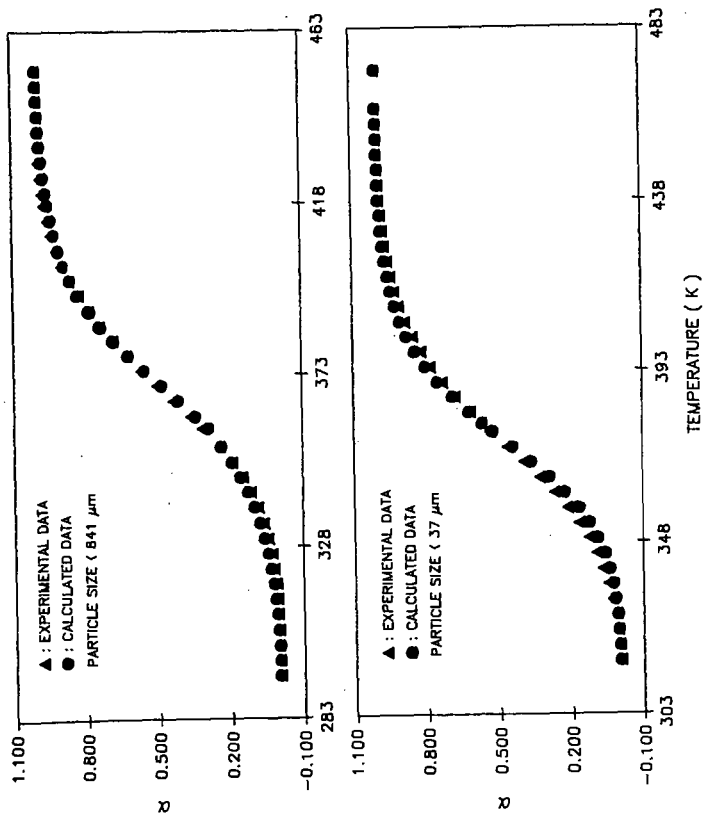


Fig. 2 This graph compares the experimentally observed desorption of water data with calculated values of Eq. 7.

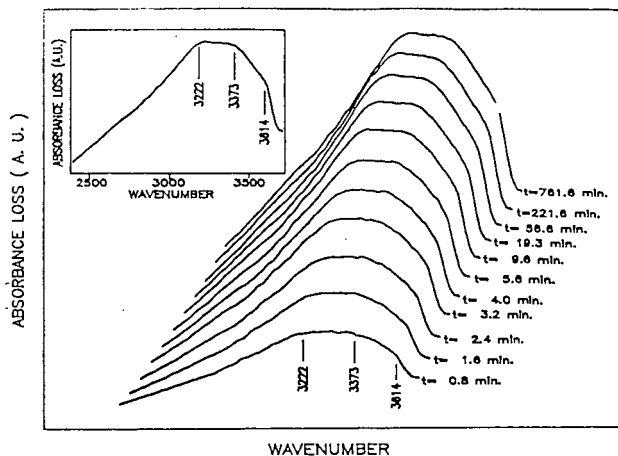


Fig. 3 FTIR difference spectra at t min. show the desorption kinetics of various types of water from < 37 particle size Beulah-Zap lignite coal in the water's stretching region.

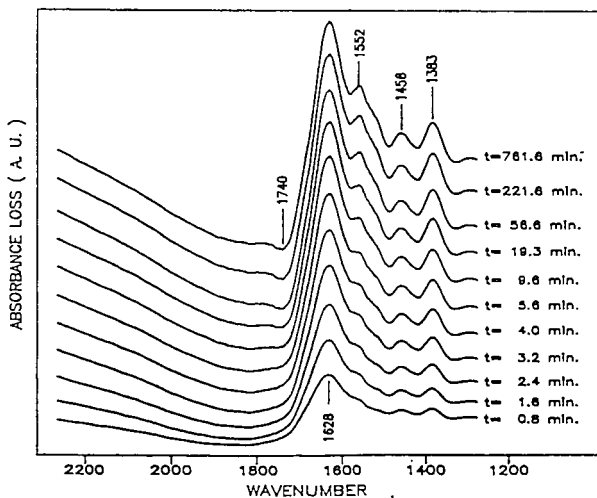


Fig. 4 FTIR difference spectra at t min. show the desorption kinetics of water from the lignite coal in the water's bending region.

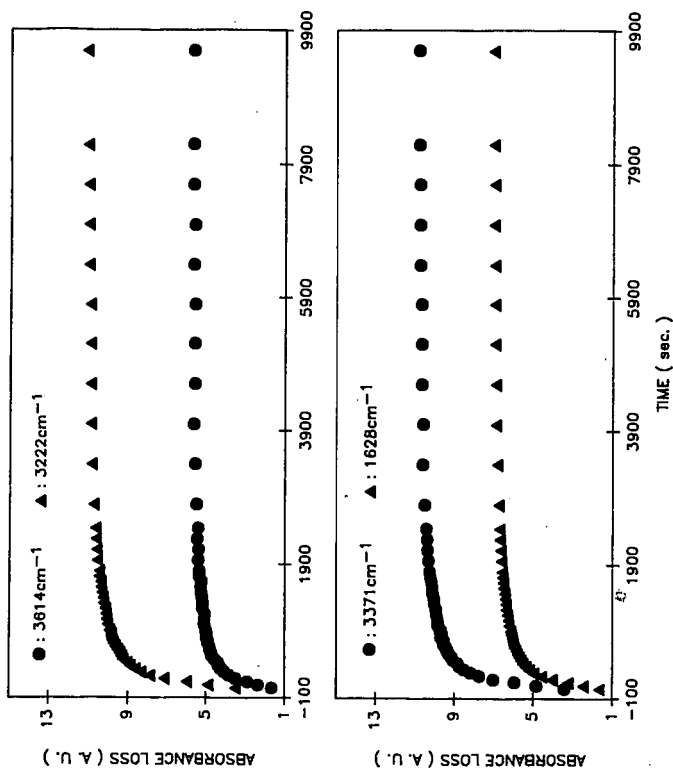


Fig. 5 Isothermal desorption kinetics of 3614, 3371, 3222, and 1628 cm^{-1} bands measured by monitoring the absorbance loss generated from difference spectrum at (t-0) min.

Lignite Dried in N₂, 20 C, -20 mesh

NDRY14D2, 20 second intervals

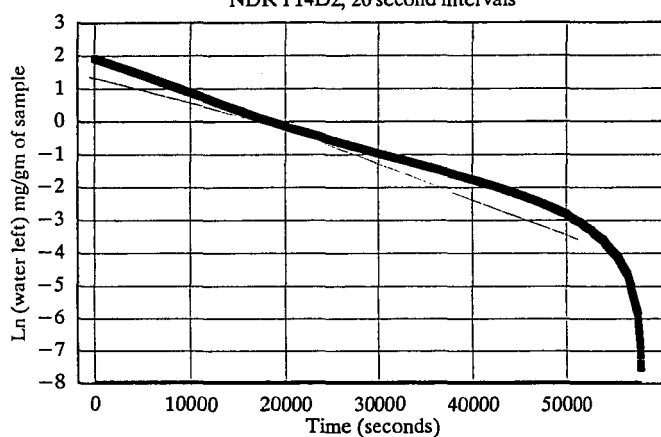


Figure 6. Typical Isothermal Thermogravimetry Run. Note two segments at different slopes after about 85% moisture loss.

**HOT-WATER UPGRADING OF LOW-GRADE COAL: FUNDAMENTALS
AND SLURRY RHEOLOGY**

vvv

M. Rashid Khan and Todd Potas*
Texaco Research & Development,
P.O. Box 509, Beacon, NY 12508

*The University of North Dakota, Energy & Environmental
Research Center, Grand Forks, ND 58202

ABSTRACT

Extensive bench-scale and pilot-plant studies have been conducted to better understand the fundamentals of hot-water drying of coal and the rheology of treated coal-water slurry. There was an increase in the heating value of the hot-water dried coal via decarboxylation. The formation of tar and extractables reduces the surface area and accessibility of water into the coal structure. As a result of decarboxylation and tar formation, the treated coal becomes relatively more hydrophobic. The slurry prepared from the hot-water dried coal was highly stable towards settling. The moisture reabsorption for the hot-water dried coal was minimal. Finally, the energy density of the slurry prepared from the hot-water dried coal approached those prepared from bituminous coals.

INTRODUCTION & BACKGROUND

The use of coal via gasification offers an excellent avenue to generate electric power with an increased efficiency for both energy recovery from coal as well as removal of pollutants (i.e., sulfur and nitrogen containing species). High-temperature pressurized, entrained-flow gasifiers (such as those used in The Texaco Coal Gasification Process) offer attractive options for integrated gasification combined cycle applications due to their high-throughput and low-level of contaminant production.

In many coal utilization processes, coal-water slurry fuel is used (1-5). Transport of coal into the gasifier by slurrying it with water offers several advantages: (a) the pumping technologies are proven and reliable, valves and flow measurement devices can be used; (b) the slurry feed is homogeneous, predictable and safe; (c) the presence of water in the slurry acts as a temperature moderator; resulting in reduced thermal wear. The high inherent moisture of low-rank coal (LRC), however, prevents the formation of coal slurry with high solids content needed for efficient operation. This necessitates a method for preparing a slurry that is pumpable and still contains high energy density (i.e., solids content) to permit gasification at a reasonable rate of oxygen consumption. This implies the need to irreversibly reduce the moisture content of the coal.

Hot-water drying (also known as "hydrothermal treatment" or "wet carbonization") of coal, initiated several decades ago (6-9),

offers an excellent avenue to efficiently achieve the objectives of a suitable slurry for gasification. The aim of this study is to review the fundamental aspects of hot-water drying of low-rank coals.

EXPERIMENTAL

Hot-water drying of coal was conducted in various reactors: batch autoclave reactors, and a continuous thermal treatment reactor. One of the batch reactors consists of a 3.8 liter electrically heated autoclave and numerous thermocouples and pressure transducers. The unit was designed so that the reactant materials could be charged rapidly into a preheated autoclave from a piston-type accumulator. This allowed the charge materials to reach operating temperature in the relatively short time of 5 to 10 minutes. It also allowed for close control of residence times as the entire contents of the autoclave reactor charged into a 7.6 liter quench vessel at room temperature to end the drying and pyrolysis reactions rapidly. After quenching, the evolved gases were vented through cold traps (and were metered and analyzed). Description of the continuous thermal treatment reactor is presented elsewhere (4,5).

RESULTS & DISCUSSION

Influence of Pretreatment Temperature/Residence Time: For a given viscosity, the dry-solids content increased with the increasing processing temperature. The viscosity versus solids contents for slurries made from treated (at various temperatures) Indian Head Lignite is shown in Figure 1. At a viscosity of 800 cP, the

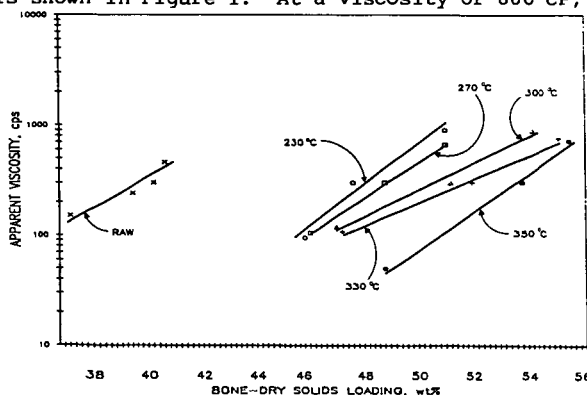


Figure 1. Apparent viscosity at 410 s^{-1} and 28°C versus solids content for coal/water slurry prepared from Indian Head Lignite before and after hydrothermal treatment

solids content increased from 42.5% to 55.5% (at a shear rate of 410 sec^{-1} at 28°C) after processing at 350°C . In addition, the higher the pretreatment temperature, the higher the solids contents, for a given viscosity of 800 cP. The slurry energy content also increased by pretreatment at 330°C (1,4).

As a result of pretreatment at 330°C , the slurry prepared from Indian Head lignite contained 150 percent of the heat content of the raw slurry. An increase in pretreatment temperature resulted in an increase in heating values for all coals (Figure 2), although to a lesser extent for higher rank coals. The influence of residence time of pretreatment on the slurry solids content is shown in Figure 3. The longer the residence, the greater the slurriability of the products. An increase in pretreatment temperature also reduced the equilibrium moisture content for all coals (Figure 4), measured soon after pretreatment.

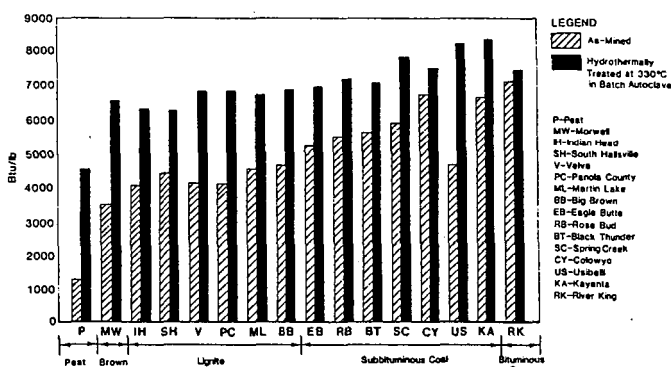


Figure 2. Slurry heating value (dry-basis) of raw and 330°C treated coal at maximum solids concentration.

Influence of Coal Type: The lower the rank of the coal, the greater the reductions in equilibrium moisture content (Figure 4) upon pretreatment. This effect is attributable to the higher concentrations of oxygen functional groups and the associated water molecules present in the lower rank coals.

The changes to the coal structure as a result of hydrothermal treatment were irreversible, and the coal maintained a low equilibrium moisture content in either air or water, unlike the untreated coal.

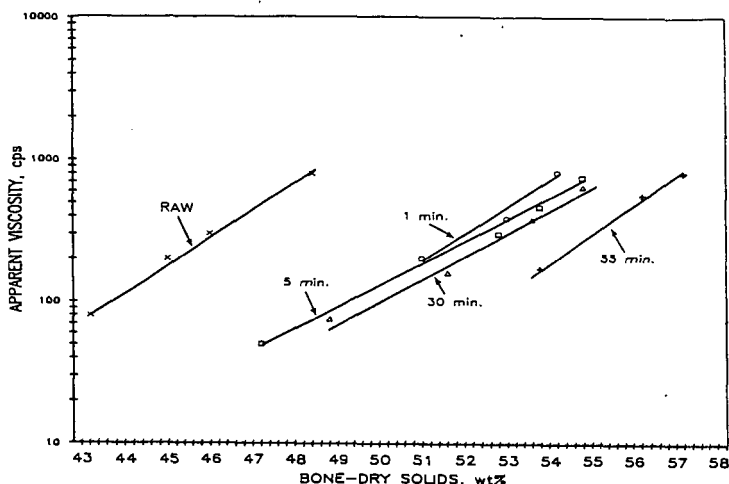


Figure 3. Apparent viscosity versus solids content for a subbituminous coal (Spring Creek, Montana) processed at 330°C at various residence times in a continuous reactor.

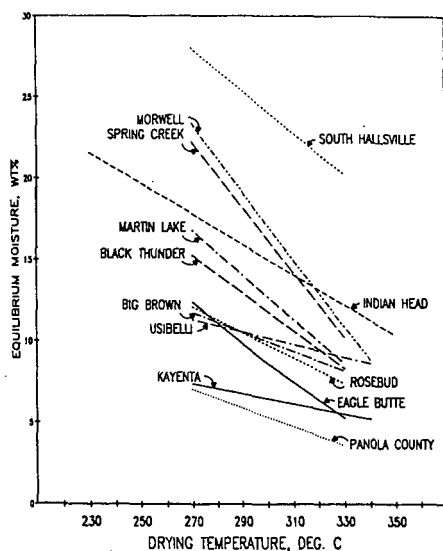


Figure 4. Equilibrium moisture versus pretreatment (hot-water-drying) temperature of various coals.

CP/MAS: Cross Polarization/Magic Angle Spinning (CP/MAS) Solid State ^{13}C -NMR spectroscopy provided interesting results on the effects of hot-water drying on the structure of the processed coal. Spectra for as-received and the hydrothermally treated coals (at 330°C , Indian Head lignite) are shown in Figure 5. The raw lignite contained large quantities of aliphatic material, long chain waxes and alkanes. However, when the coal was hydrothermally treated at 330°C there was a dramatic reduction in these groups, perhaps as a result of cracking and extraction. Many coals examined exhibited a significant weight-loss due to expulsion of carboxylic groups during thermal treatment. The carboxylic groups, unlike aliphatic compounds, do not contribute significantly to the heating value of coal. Thus, the loss of these oxygenated functional groups actually enhances the energy density of the product.

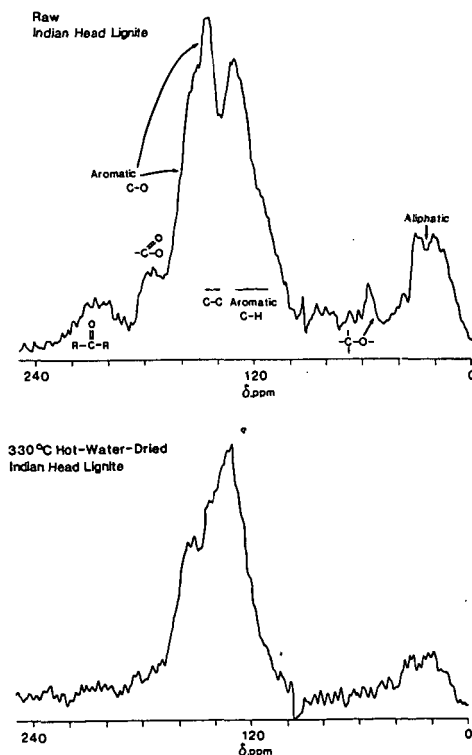


Figure 5. Solid-state ^{13}C NMR spectra for as-mined and 330°C hot-water dried Indian Head (North Dakota) lignite.

Evolved Products: Table 1 provides additional data on the influence of pretreatment temperature on coal structure, and on the nature of the evolved products as a result of heat-treatment. After hydrothermal treatment of Indian Head Lignite at 340°C, the yield of phenolics, alcohols and hydrocarbon gases represented less than 1 wt% of the raw maf coal, while the yield of decarboxylation products (CO₂, CO and H₂O) represented nearly 18% of the products. Decarboxylation of coal had a major effect on reducing the hydrophilic nature of coal, as reflected by the decreases in the equilibrium moisture content.

Formation of Extractables: A significant impact of hydrothermal-treatment was also reflected in the exuded tar yield from the treated coal. The yield of extractables (tar) was significantly increased as a result of hydrothermal treatment (Figure 6). The

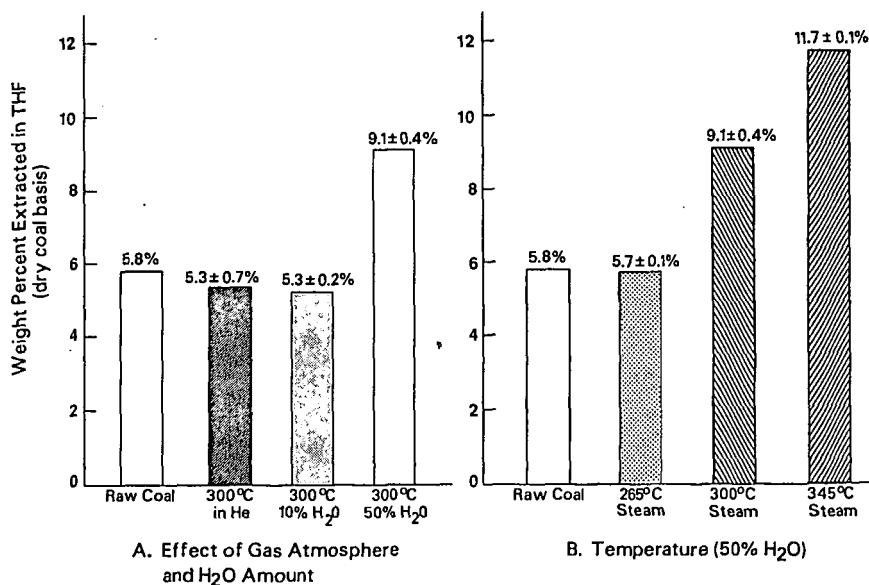


Figure 6. Effect of hot-water-drying of coal on extractable yield

Table 1

COMPARISON OF MATERIAL BALANCE RESULTS FOR HYDROTHERMALLY
TREATING INDIAN HEAD LIGNITE IN A COLD-CHARGE AUTOCLAVE

Coal	Indian Head				
	231	272	302	333	348
Process Temp., °C	400	900	1,400	2,300	2,500
Process Pressure, Psig					
Net Yields - wt% maf coal ^a					
Decarboxylation and Dehydration Products (CO+CO ₂ +H ₂ O)	1.6	9.8	13.8	14.8	17.5
Pyrolysis Product Gases (H ₂ +C ₁ -C ₄ +H ₂ S+NH ₃)	0.0	0.0	0.2	0.2	0.1
Pyrolysis Product Liquids (Phenols, Methanol, Acetone, MEK)	0.0	0.2	0.4	0.4	0.8
Residual maf coal	98.1	92.2	87.7	85.9	83.1
Energy Recovery, %	100.0	98.2	97.8	98.4	96.6
Product Coal Characteristics					
Heating value, mf basis, Btu/lb	10,400	10,800	11,200	11,400	11,600
Equilibrium Moisture, wt %	20.9	18.0	14.5	13.5	7.4
lbs ash/MM Btu	14.83	13.28	13.44	13.93	14.02
lbs sodium/MM Btu	0.53	0.47	0.42	0.42	0.27
lbs sulfur/MM Btu	1.03	0.98	1.00	1.02	0.94
Coal-Water Slurry Properties ^b					
Maximum measured solids concentration, wt%	51.0	50.9	54.2	55.3	55.6
Apparent viscosity, cps					
at 100 sec ⁻¹ and 28°C	1,770	1,530	1,280	1,420	1,190
at 410 sec ⁻¹ and 28°C	890	650	860	740	710
Heating value, Btu/lb	5,300	5,500	6,070	6,300	6,450

^aNet yields do not total 100% because of errors introduced by the changing inorganic content of the coal and the changing ways it behaves when samples are ashed.

^bThe data shown is for samples which were first filtered without washing and then reslurried in deionized water. For some coals significant improvements were seen when the filter cake was washed.

yield of tar was quantified by extracting the treated coal with tetrahydrofuran (THF), as described elsewhere (3). For the Illinois No. 6, the yield of extractables increased significantly with the increase in pretreatment temperature. The influences of gas atmosphere (amount of water) and temperature of pretreatment are shown in Figure 6.

Surface Area of Treated Products Compared to Feed: An important change involved the sealing of the coal pores which exuded the tar. The influence of tar condensation on coal pores (and openings) and surfaces resulted in a decrease in the surface area (i.e., accessibility) as well as the hydrophilic nature of coal. As a result, the surface area of the hot-water dried coal decreased by 30 to 40%, as determined by BET (Brunauer, Emmett, and Teller) approach.

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TEMPERATURE AND HIGH SHEAR VISCOSITY ON THE HANDLING
OF COAL-WATER SLURRIES

Frank Ohene, Keith Bowman, Antonio Williams and Bryan Obonna
Chemistry Department, Grambling State University
Grambling, La 71270

and
John P. Doohar
Physics Department, Adelphi University
Garden City, NY 11530

ABSTRACT

An experimental study of the effect of high shear rheology and temperature on coal-water slurry, (CWS), was studied. Slurries for this study were formulated in our laboratory from four different coals, ranging from subbituminous western coal to eastern bituminous coals in order to gain a broader understanding of the CWS behavior. All the slurries exhibited a non-Newtonian flow and the packing efficiency of the particles was found to govern the slurry behavior.

(Key Words: rheological, viscosity, particle size distribution)

INTRODUCTION

Coal-Water Slurries have the potential of a near-term replacement for fuel oil [1]. The fundamental understanding of the preparation and handling of highly loaded CWS with low viscosity and desirable atomization and combustion properties is necessary in the commercialization of the CWS [2].

The design of flow systems of suspensions with high solids content such as Coal-Water Slurries, require a detailed rheological knowledge of the suspension [3]. Mathematical models such as Bingham plastic model, Power law model, or H.-Bulkley model have been used to define the flow properties of such suspensions [4,5]. For most suspensions however, the governing parameters have to be determined experimentally. This is due to the variability in characteristics such as the particle size distribution, shape of the particles, concentration of solids, surface chemistry of the particles, and dispersants used to stabilize the suspensions [6,7].

Solids concentration and particle size have been recognized as important hydraulic variables and particle size distribution (PSD) is of considerable importance in CWS formulation [8]. However, no universally acceptable method for its incorporation into models and correlations has been established. Thus, the specific influence of the various particle size fractions on the rheology of CWS continue to receive attention.

This paper reports the results of an experimental technique of examining the various particle size fractions on CWS rheology, using a combination of a Haake RV-20 concentric cylinder viscometer and an Extrusion Rheometer.

EXPERIMENTAL

The coals used in all the experiments were from the Pennsylvania State University Coal Data Bank. The Proximate and Ultimate analyses of the coals are as shown in Table 1.

The coal samples were ground to a distribution as shown in Figure 1 and carefully screened to obtain size fractions of: -400 mesh, +400/-325 mesh, +325/-270 mesh, +270/-200 mesh and +200/-100 mesh using standard U.S sieve screens. Slurries were prepared from blended distributions as shown in Table 2 and using either an ammonium naphthalene sulfonate (A-23) or Igepal 990 as an additive. Each slurry was made using a dosage of 0.3% dispersant based on dry coal and at a pH of 10. The packing concentrations were calculated from particle size distribution measurements obtained by using a Microtrac Particle Size Analyzer Model 2600, and a program based on truncated log-normal distribution which has been developed at the Adelphi Center for Energy Studies. The packing concentrations calculated increased with increase in the number of fines (-325 mesh) to a value of 40 % fines by weight. Above a value of 40% fines, the packing concentration decreased.

Rheological Testing

A Haake RV-20 concentric cylinder viscometer and an Extrusion Rheometer were used to determine the rheological properties of the CWS at low and high shear rates. In The RV-20, the slurry is sheared in the annular gap between a rotating bob and a stationary cup. The torque necessary to rotate the bob at a given speed is measured by a torsion spring. The drive unit consists of a driving motor, a tachometer-generator, and a reduction gear. The stator is surrounded by a temperature tempering vessel (enclosed in a steel container to prevent moisture loss) connected with a constant temperature bath. The temperature can be controlled to $\pm 0.01^\circ\text{C}$.

The viscometer is integrated with an IBM ps/2 data acquisition and analysis system. The signals from the viscometer is monitored twice per second and converted to torque and rotational speed values. Viscosity as a function of shear rate was computed using one of the following flow models:

$$\tau = \tau_0 + \mu_p \dot{\gamma} \quad (\text{Bingham law}) \quad (1)$$

$$\tau = K \dot{\gamma}^n \quad (\text{Power law}) \quad (2)$$

$$\tau = \tau_0 + K \dot{\gamma}^n \quad (\text{H.-Bulkley law}) \quad (3)$$

Where:

τ_0 is the yield value

K is the flow consistency number

n is the flow behavior index.

$n = 1$ for a Newtonian flow

$<$ for a pseudoplastic material

and $>$ for a dilatant material.

Figure 2 shows a typical flow curve for a CWS formulated at 65% solids content generated in this viscometer. The shear rate, to which the sample was subjected, was continuously increased from zero to a maximum determined by the viscosity of the CWS (curve 1). Curve 2 decreased to zero, curve 3 increased to a maximum, and curve 4 decreased to zero. The viscosity measurements were taken from curve 3, which represents the fluid

after it has been sheared and its structure broken down.

RESULTS AND DISCUSSION:

Effect of Particle Size Distribution on Rheology of CWS.

Figure 3 shows the effect of particle size distribution on the flow behavior of the slurries. Table 3 lists the rheological data evaluated from these flow curves. The particle size distribution was formulated according to the information contained in Table 2, and all the slurries contained 65% solids content and 0.3% A-23 dispersant.

Rheological analyses of the flow curves show that the flow behavior changed from dilatant to pseudoplastic as the packing concentration increased. Also, the viscosity was found to decrease with increase in the packing concentrations of the slurries. This is an indication that a wider distribution is indeed necessary for more efficient packing.

Effect of Shear Rate on Flow Behavior

Figure 4 is the flow behavior of 63% solids loading of the four coals listed in Table 1. Their rheological properties are listed in Table 4. All the samples exhibit a pseudoplastic behavior with yield at this slurry concentration. PSOC-1493 and 1494 however, have higher yield values and viscosities relative to PSOC-1487 and 1475.

Previous studies on the effect of coal properties on slurry quality show that the acidic functional groups on the coal surface as well as the equilibrium moisture content of the coal samples have an adverse effect on the slurry quality [9,10,11]. ESCA analysis of these samples show a higher degree of carboxylic functional groups on PSOC-1494 and 1493 relative to PSOC-1475 and 1487. The differences in the flow patterns observed may be due to their characteristic properties.

High shear Rheology of 65% solids content of PSOC-1475 was determined using an Extrusion Rheometer. This device determines the apparent viscosity of the slurry under flowing conditions. The CWS volume flow rate, Q , and pressure drop, ΔP , were measured for laminar flow through a tube of Length, L , and radius, R . The shear stress, τ_p , and the shear rate, $\dot{\gamma}$, were obtained from the pipeline flow data as follows:

The shear stress at the pipe wall, τ_p , can be defined as:

$$\tau_p = \frac{R}{2} \left(\frac{\Delta P}{L} \right) \quad (4)$$

against a pipe flow characteristic, Γ , given by:

$$\Gamma = \frac{4(Q)}{\pi R^3} \quad (5)$$

where $\Delta P/L$ is the pressure gradient along the tube of length, L
 Q is the volumetric flow
 and R is the tube inside radius.

Γ relates to γ through the Rabinowitsch-Mooney relation [12]:

$$\gamma_p = (1/4)\Gamma[(3+(d \ln \Gamma / d \ln \gamma_p))] \quad (6)$$

The apparent viscosity of the suspension then is given by

$$\eta = \tau_p / \gamma_p \quad (7)$$

The data obtained from the Extrusion Rheometer are shown in Table 5. Figure 5 is the rheogram generated from this data. Rheological analysis shows that the rheogram can be described by the relation:

$$\tau = 1.4 + 0.84 (\gamma')^{0.76} \quad (8)$$

The apparent viscosities of the slurry as a function of shear rate are listed in Table 6. There is a decrease in viscosity with increase in shear rate to a value of 4000 s^{-1} due to the existence of yield stresses, but the viscosity remains fairly constant after a shear rate of 4000 s^{-1} .

Effect of Temperature

The variation of viscosity of 67% solids of PSOC-1475 as a function of temperature is shown in Figure 6. The viscosity of CWS was found to decrease with increase in temperature between 19°C and 50°C . However, with Igepal 990 as an additive, there was an increase in viscosity between 45°C and 60°C . It is apparent that the flow behavior of the slurry in the low temperature range is governed by the behavior of water. Above 45°C , the flow behavior is dependent on the additive. The change in flow behavior can be caused by changes in the solubility behavior or changes in the interaction of the additive with the coal particles at higher temperatures [13]. This may explain the increase in viscosity with increase in temperature when Igepal 990 was used as a dispersant.

The high temperature behavior of CWS is of interest with regard to their atomization behavior. Thus, CWS prepared using Igepal 990 as an additive will require special handling techniques at higher temperatures.

CONCLUSION

An experimental technique of examining the influence of particle size distribution and high shear rheology of CWS has been made. The results of the study indicate a range of rheological behavior depending on solids content, particle size distribution, and coal type. Solids with low packing efficiency have relatively high time-independent yield points and also have high viscosities at a shear rate of 100 s^{-1} .

Slurries prepared from coals with low moisture content however, have low time-independent yield values compared to slurries prepared with high moisture content.

The behavior of a slurry at high temperatures is dependent on the additive type. With Igepal 990 as an additive, the slurry viscosity increases with increase in temperature indicating that preheating of such a slurry may present handling problems.

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Table 1

Proximate and Ultimate Analyses Of Coal Samples.

	PSOC-1494 Kentucky #9	PSOC-1487 Adaville#1	PSOC-1493 Illinois#6	PSOC-1475 Elkhorn#3
<u>Proximate Analysis</u>				
% Moisture	7.12	18.99	9.43	3.37
% Ash	10.97	4.55	13.74	3.22
% Volatile	35.77	34.67	34.34	36.03
% Fixed Carbon	46.14	41.78	42.50	57.38
<u>ULTIMATE ANALYSIS</u>				
% Ash	10.97	4.55	13.74	3.22
% Carbon	65.32	57.96	59.98	78.38
% Hydrogen	3.98	4.09	3.74	5.20
% Nitrogen	1.14	0.84	1.15	1.44
% Total Sulfur	4.50	1.06	4.51	0.95
% Oxygen	6.97	12.50	7.41	7.45
C/O	9.37	4.64	8.09	10.45
FC/VM	1.29	1.21	1.24	1.59
HG Index	72.00	61.10	62.20	58.70

Table 2

Weight Fractions And Packing Concentrations

WT %>200 MESH	WT% -200/325 MESH	WT %<325 MESH	PACKING CONCENTRATION
53.7%	8.5%	37.8%	83.4%
47.7%	9.4%	42.9%	83.1%
41.7%	9.0%	49.3%	83.6%
43.6%	9.4%	47.0%	76.4%
53%	8.3%	39.7%	85.3%
36.2%	15.4%	48.4%	72.1%
26.5%	18.1%	55.4%	73.4%
9.6%	15.6%	74.8%	69.6%
58.1%	2.2%	39.7%	85.2%

Table 3

Rheological Properties Of 65% (PSOC-1475) CWS
With Varying Packing Concentrations.

PACKING	n	τ_0	K	R^2	η_{100} (mPas)
69.6	1.036	3.25	0.276	0.99	335
72.1	0.970	2.01	0.340	0.97	320
73.4	0.907	1.76	0.322	0.98	301
76.4	0.884	4.10	0.827	0.97	248

Table 4

Rheological Properties of 63% CWS.

Sample	n	τ_0	K	R^2	η_{100} (mPas)
1494	0.680	24.0	0.676	0.86	445
1493	0.729	11.3	1.42	0.98	527
1487	0.913	0.250	0.879	0.93	293
1475	0.916	0.082	0.238	0.99	180

Table 5

Extrusion Rheometer Flow Data.

Weight of Slurry/s	Pressure (psig)	Shear Rate(s^{-1})	Shear Stress(mPa)	Viscosity mPa.s
1.6195	10	1181	7860	665
2.55	20	1866	15721	642
5.4995	30	4008	23581	588
7.3921	40	5391	31441	583
9.999	50	7292	39302	539
11.615	60	8471	47162	557
14.237	70	10383	55022	530
15.4417	80	11262	62882	558
17.4041	90	12692	70743	557
20.2955	100	14801	78603	531

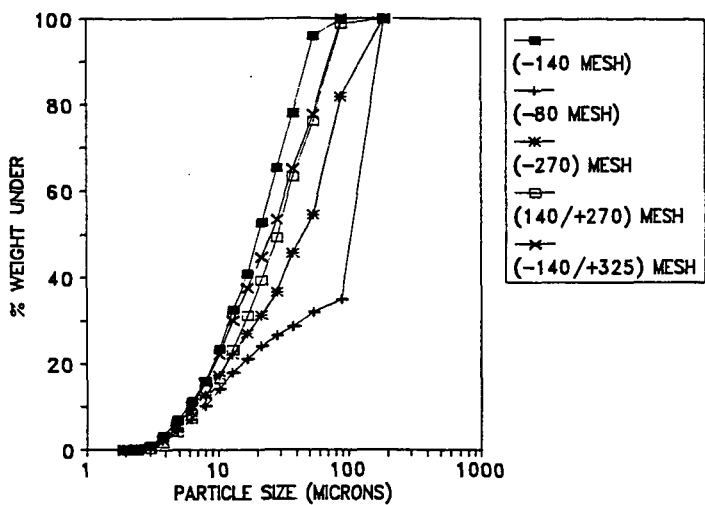


FIGURE 1. PARTICLE SIZE DISTRIBUTION

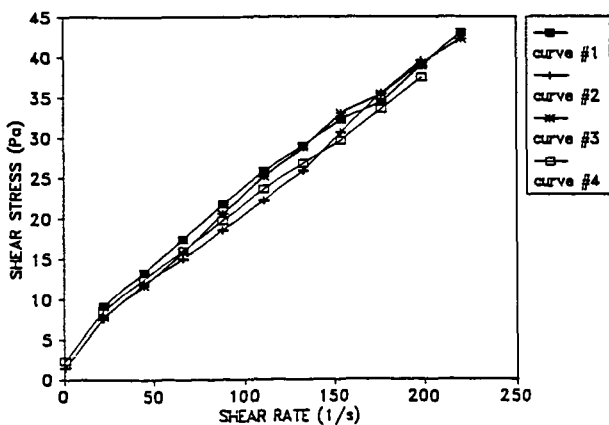


FIGURE 2. FLOW CURVE OF 65% CWS.

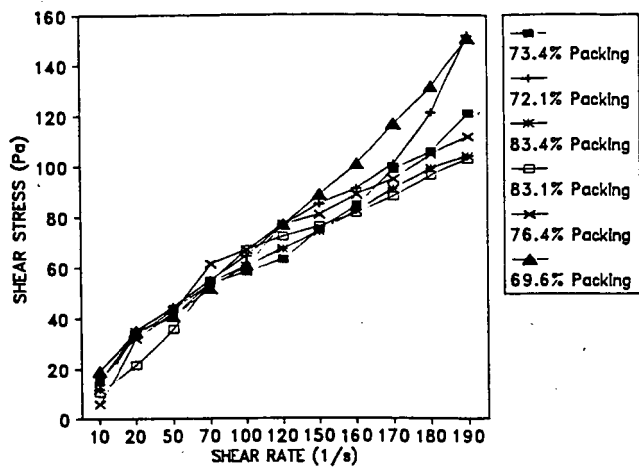


FIGURE 3. THE EFFECT OF PARTICLE SIZE DISTRIBUTION ON THE FLOW BEHAVIOR OF 65% CWS

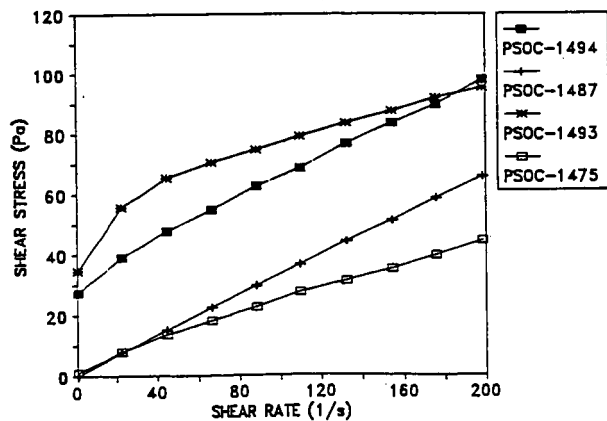


FIGURE 4. VARIATION OF VISCOSITY AS A FUNCTION OF TEMPERATURE

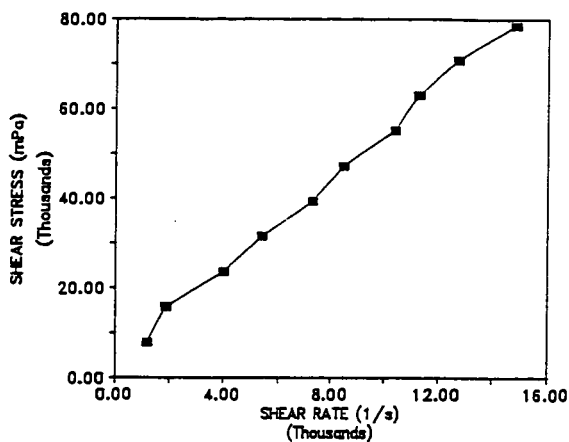


FIGURE 5. A RHEOGRAM GENERATED FROM AN EXTRUSION RHEOMETER DATA

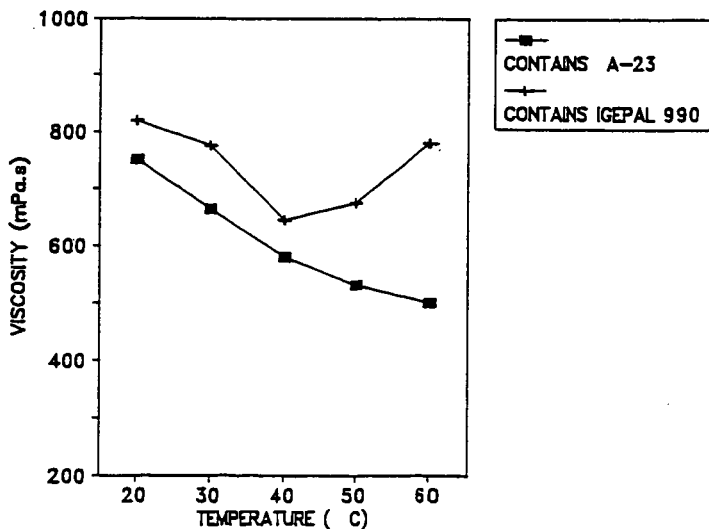


FIGURE 6. VARIATION OF VISCOSITY AS A FUNCTION OF TEMPERATURE

ENHANCED COAL HYDROGASIFICATION VIA OXIDATIVE PRETREATMENT

Martin E. Toomajian, Michael G. Lussier, and Dennis J. Miller
Department of Chemical Engineering
Michigan State University
East Lansing, MI 48824.

Key Words: Hydrogasification, Pretreatment, Oxidation

INTRODUCTION

Coal hydrogasification is not commonly viewed as a competitive route to gaseous fuels and thus has not been studied as extensively as steam gasification. Relative to steam gasification, hydrogasification requires higher pressures to make the reaction thermodynamically favorable; more importantly, hydrogen is presently too expensive to be considered a viable reactant for large-scale coal conversion. Hydrogasification is, however, a useful research tool for improving the understanding of other coal gasification processes. Further, hydrogasification is the primary reaction in at least one coal conversion process, the HYDROCARB process [1], and could be an important means of enhancing methane yields in gasification processes such as that developed by Exxon [2].

The reaction of carbon with pure hydrogen offers a unique opportunity to study the role of oxygen in gasification, since any oxygen present during gasification must be initially associated with the solid. Generally, oxygen is present in bulk carbon and as chemically-bound functional groups on the carbon surface. The desorption of these functional groups as CO or CO₂ may be the rate-limiting step in oxidative gasification; desorption also leaves "nascent", or reactive, sites at which further reaction occurs [3]. Thus, oxidizing the carbon surface prior to conversion should increase the concentration of active sites for gasification.

Exposure to molecular oxygen and immersion in concentrated nitric acid are two common methods of oxidative pretreatment of carbonaceous solids. Partial combustion in oxygen may convert some carbon and open new pore structure, while HNO₃ pretreatment does not significantly alter total surface area or carbon structure [4].

For steam and CO₂ gasification, it has been shown that oxidative pretreatment enhances both catalyzed and uncatalyzed gasification rates. In uncatalyzed gasification, Keleman and Freund [5] determined that prior oxidation of a glassy carbon enhances the dissociative adsorption of O₂ and CO₂ on the surface, thus enhancing gasification rate. In catalyzed gasification, Mims and Krajewski [6] determined that catalyst activity is related to the presence of surface oxygen groups. Keleman et al. [7] and Saber et al. [8] showed that surface oxygen groups have a stabilizing effect on alkali salt catalysts and aid in activating the catalysts. Finally, Ohtsuka et al. [9] found that HNO₃ pretreatment increases the gasification rate by six-fold.

The presence of oxygen also strongly affects hydrogen gasification rates. Cao and Back [10] determined that adding 0.1% oxygen to hydrogen increases the rate of methane formation by an order of magnitude, and Blackwood [11] reported that hydrogasification rate depends on oxygen content of the reacting wood char. Otake and Jenkins

[12] showed that methane formation is directly related to desorption of oxygen complexes as carbon monoxide.

Previous work in our laboratory with model carbons [13,14] illustrated that pretreatment via partial combustion produces up to a two-fold increase in uncatalyzed hydrogasification rate. Also, HNO_3 oxidation results in as much as a three-fold enhancement of the K_2CO_3 -catalyzed rate and a lesser (50%) increase in the uncatalyzed rate. Based on the work of Walker [3], Zoheidi [15] postulated that desorption of oxygen groups occurs during heatup. This desorption creates reactive sites at which hydrogen attacks to form methane. Treptau and Miller [14] used x-ray photoelectron spectroscopy to verify that surface oxygen groups desorb before gasification temperatures are reached.

In this paper, we present initial results of oxidative treatment of coal char for the purpose of enhancing hydrogasification rates and overall conversion of coal to methane. Oxidation both before and during the course of carbon conversion is investigated.

EXPERIMENTAL

A coal char, a demineralized coal char, and a Saran char were used as solid reactants in this study. The coal chars were prepared from an Illinois #6 coal (PSOC 1493), and the Saran char was prepared from Saran (Dow MA 127) resin powder. Ultimate analysis of the three chars are given in Table 1.

The chars were prepared by heating coal or Saran resin in a 4.8 cm ID quartz tube furnace under nitrogen at $100^\circ\text{C}/\text{min}$ to 900°C and holding for 30 minutes. A portion of the coal char prepared was then demineralized by contacting repeatedly with concentrated HF and concentrated HCl at $55\text{--}60^\circ\text{C}$, vacuum drying in nitrogen at 110°C , and then reheating under nitrogen to 900°C to remove residual volatiles. A sample of each of the three chars was loaded with 10 wt% K_2CO_3 by drying a slurry of char and K_2CO_3 solution at 90°C for several hours.

Oxidative treatments were performed prior to gasification and following partial gasification in hydrogen by exposing chars to air at 375°C in the quartz tube furnace. For oxidation prior to gasification (preoxidation), approximately five grams of char were oxidized in an air flow of $50\text{cc}/\text{min}$. For oxidation following partial gasification, char samples were removed from the gasification reactor, placed in the quartz tube furnace, and oxidized in stagnant air.

Hydrogasification was conducted in a high temperature, high pressure, differential flow reactor. The pressure vessel, furnace, gas collection system, and gas analysis system are all described in detail by Zoheidi [15] with the exception that a Varian Model 3300 Gas Chromatograph is now used for gas analysis. Samples were gasified at $700\text{--}800^\circ\text{C}$ in 500 psi pure hydrogen. Rates were measured by timed collection of product gases.

Char samples were analyzed via several procedures both before and after gasification and oxidative treatment. X-ray photoelectron spectroscopy (XPS) was used to determine the surface concentration of oxygen on samples treated at different temperatures and reactor conditions. A vacuum pretreatment reactor [14] enabled us to heat samples to 1000°C under high vacuum or in the presence of reactant

gases. Samples were transferred to the XPS instrument (PHI Model 5400) using a vacuum transfer vessel to avoid sample contamination.

A high pressure Sartorius microbalance was used to determine the total surface area by carbon dioxide adsorption. Prior to CO₂ introduction, the system was evacuated to a pressure of less than one Torr and samples were heated to 150 °C until no further weight loss was observed. The sample was then cooled to room temperature and carbon dioxide pressure was increased incrementally while the sample weight gain was recorded. The Dubinin-Radushkevitch method [16] was used to calculate the total surface area.

Sample pH was determined as a measure of the type of surface oxygen groups present in a manner similar to the ASTM standard method [17]. The char samples were wetted in a 0.1 molar potassium chloride solution and boiled under reflux for 2 hours. A standard 0.1 molar KCl solution was boiled concurrently with the char suspension. The solutions were then cooled to room temperature and the pH of each measured using a Fisher Scientific Accumet 950 pH/ion Meter. The difference in pH between the sample and the standard determines the nature of the surface oxygen groups: a positive change indicates basic groups and a negative change results from acidic surface groups.

RESULTS

The absolute rates reported in the figures for hydrogasification are based on initial mass of carbon in the sample as determined by ultimate analysis (Table 1). Except for gasification of as-received coal char (Figure 2), all gasification runs were carried out for two hours at steady state conditions. Only steady state data are shown; the absence of data at low conversion is the result of carbon conversion at unsteady state.

The rate of hydrogasification of coal char sharply decreases with conversion, undergoing an eight-fold decrease over the first 20% carbon conversion. Preoxidation of demineralized char at 375°C results in up to a 6.3% wt. loss (Table 2), but it does not result in any significant enhancement in gasification rate (Figure 1) or in the total surface oxygen content as measured by XPS (Table 2). The pH measurements indicate, however, that a greater fraction of the surface oxygen groups, following oxidation, are acidic in nature (Table 2).

Results of oxidative treatment (375°C) following partial gasification are shown for coal char in Figure 2. The intermediate oxidations result in a two- to three-fold enhancement in rate upon further hydrogasification. The observed rate enhancement decays as gasification proceeds and after about 5% conversion, the rate returns to approximately that of the nonoxidized sample. Two oxidation times are presented; however, there does not appear to be any added benefit in long oxidation. A slight weight gain of the chars was recorded from the oxidation.

In Figure 3, the effect of adding K₂CO₃ (10% by weight) to coal char is presented. The presence of the catalyst significantly increases the hydrogasification rate, and intermediate oxidation of the catalyzed char results in about a 50% enhancement in rate. There was significant carbon weight loss upon oxidation (20%) so Figure 3 reports rate versus carbon conversion in gasification.

The results of intermediate oxidation of Saran char are given in Figure 4. Again, approximately a two-fold rate enhancement is observed.

DISCUSSION

In earlier work on model carbons [13,14], we postulated the active sites for methane formation are formed by desorption of oxygen functional groups. This desorption occurs during heatup to gasification temperature; Figure 5 illustrates that upon heating coal char to gasification temperature, all excess surface oxygen has desorbed. Since no oxygen is present in the reactant gas in hydrogasification, active sites can only arise from oxygen groups initially on the surface or in the bulk solid. The active sites from surface groups are consumed as carbon is converted, and gasification rate declines accordingly. This drop in gasification rate is evidenced in all results presented.

Oxidative pretreatment (Figure 1) did not result in a large increase in the gasification rate of coal char. The pretreatment had little effect because the sample was already well oxidized as evidenced by the XPS results in Table 2. Thus, few additional sites were formed via oxidation. Following partial gasification of the char, however, active sites have been consumed and the char is in a reduced state. Oxidation at 375°C then placed new oxygen groups on the carbon surface; these new groups desorb upon reheating to gasification temperature to produce active sites for methane formation. These sites are consumed as reaction proceeds and the rate decays back to that of the nonoxidized sample.

Catalyzed gasification rate enhancement from oxidation is in agreement with the results obtained by Saber et al. [8] and Keleman et al. [5] discussed in the introduction. The added stability of potassium species on the carbon surface during gasification is especially important in the reducing hydrogen environment, and thus the rate enhancement from oxidation may be greater in hydrogen than in oxidizing environments.

Changes in carbon structure and morphology occur during gasification, and thus may account for some of the observed gasification behavior. Since the coal char is heterogeneous, the most reactive carbon gasifies first; thus, the decreases in rate may arise from changes in carbon reactivity as well as loss of active sites. The gasification rate, however, is not related to the total surface area of the chars. While the rate decreases markedly, the total surface area remains essentially constant at $290 \pm 15 \text{ m}^2/\text{g}$ sample for the coal char and $750 \pm 35 \text{ m}^2/\text{g}$ sample for the Saran char over the carbon conversion range of 0% to 34%. Also, the Saran char total surface area was initially twice that of the coal char while its gasification rate was similar to that of the char. Further, total surface did not vary significantly over the course of oxidation, indicating that the rate enhancement resulted from fixation of oxygen groups and not from the opening of new pore structure.

Finally, although preoxidation of the coal char did not significantly increase the amount of surface oxygen, it did change the nature of the oxygen groups. The sample surface pH decreased by a factor of two indicating a one hundred-fold increase in surface

acidity. This fixation of acidic surface groups is characteristic of oxidation at 375°C in air. The importance of the type of oxygen group on the rate enhancement is not clear, but it is currently under investigation.

CONCLUSIONS

Oxidation via exposure to molecular oxygen enhances hydrogasification rate of coal chars and model carbons provided the char surface is not previously oxidized. Oxidation following partial gasification results in a two- to three-fold increase in gasification rate for all chars studied, while oxidation of a char previously saturated with oxygen had little effect. Work continues toward increasing rate enhancement via oxidative treatment and in understanding the importance that different types of oxygen groups have on the extent of enhancement.

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Table 1. ULTIMATE ANALYSIS OF SAMPLES
(Weight % - Dry Basis)

Element	Coal Char	Demineralized	
		Coal Char	Saran Char
C	75.30	93.01	96.36
H	.53	.27	.53
N	1.34	1.62	1.04
S	3.55	1.82	.43
Ash	17.33	2.28	.08
O (by diff)	1.95	.73	1.56
Cl	---	.25	---
F	---	.02	---
	100	100	100

Table 2. XPS AND pH RESULTS FOR DEMINERALIZED COAL CHAR
(XPS Pretreatment Temperature -->200 °C)

Char Burnoff (%)	Oxidative Pretreatment		XPS Surface	
	Treatment Time at 375°C (hr)		O/C Ratio	pH
0.0	0		.0921	0.77
2.3	120		.0971	-1.3
6.3	160		.1036	-2.8

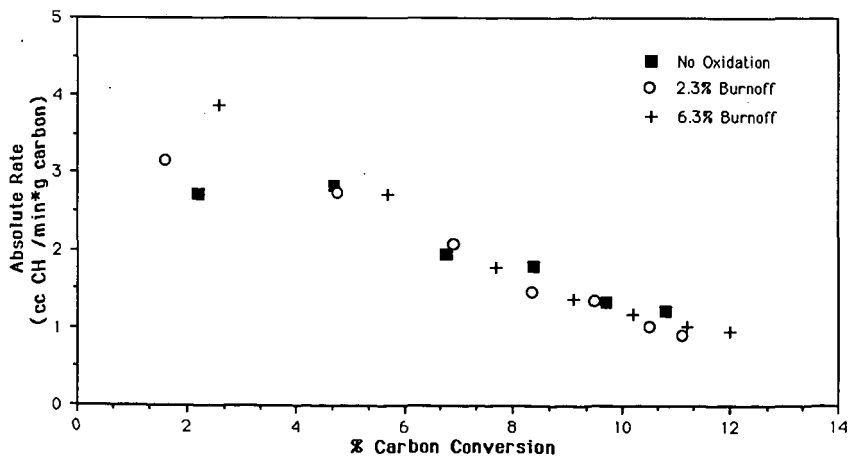


Figure 1. Effect of Preoxidation on Gasification
Rate of Demineralized Coal Char

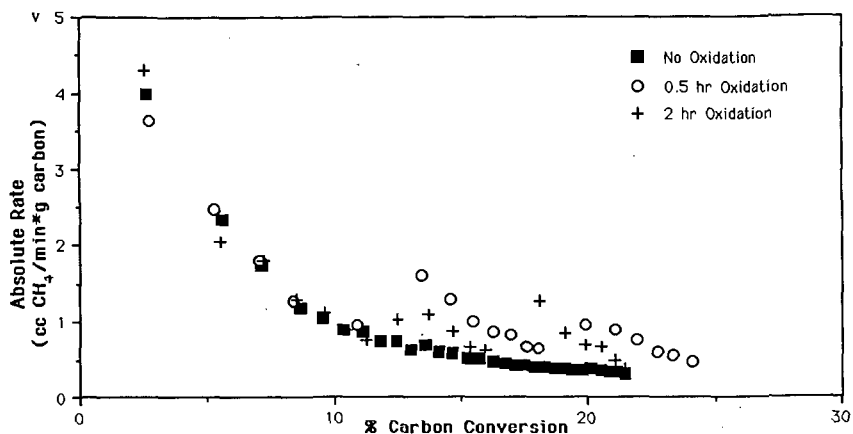


Figure 2. Effect of Two Intermediate Oxidations on the Gasification Rate of Coal Chars

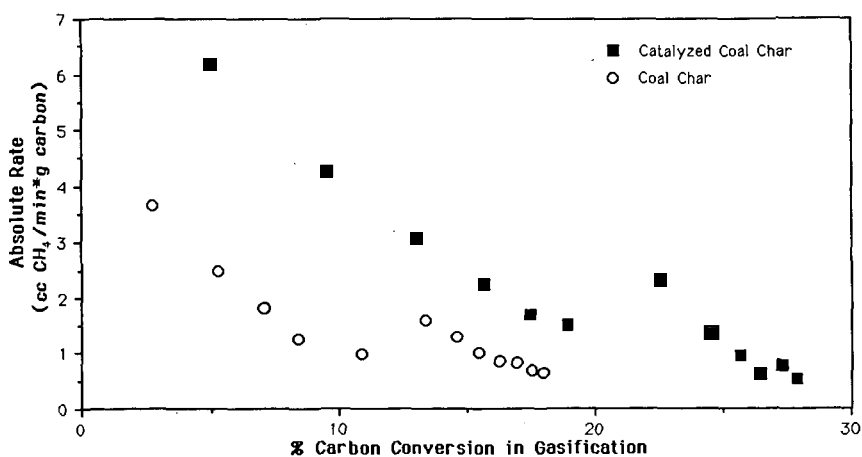


Figure 3. Effect of Intermediate Oxidation on Gasification of K₂CO₃-Catalyzed and Uncatalyzed Coal Char

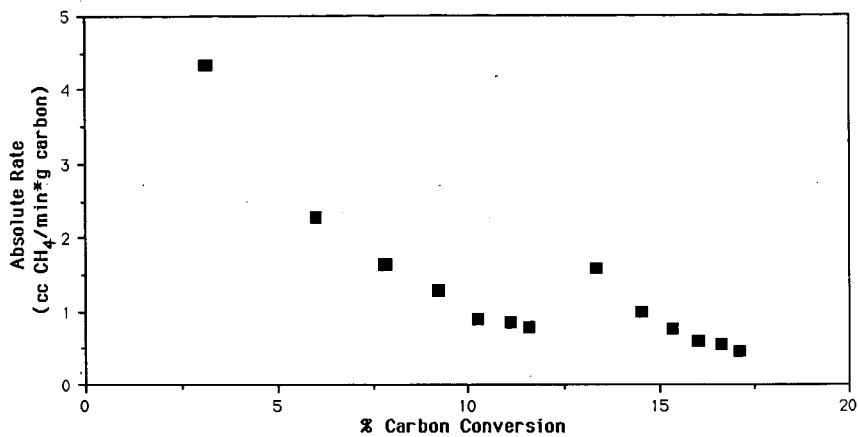


Figure 4. Effect of Intermediate Oxidation on Saran Char

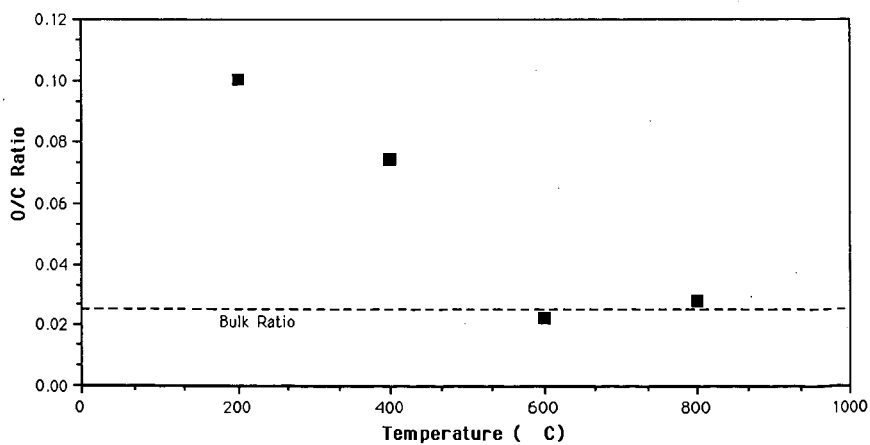


Figure 5. XPS Results for Coal Char Heated to Gasification Temperature

A MULTIPRODUCT SLATE FROM MILD GASIFICATION OF WYOMING COAL

Robert Ness, Jr., Ted Aulich, Laura Sharp, and Brian Runge
University of North Dakota Energy and Environmental Research Center
Box 8213, University Station
Grand Forks, ND 58202

Keywords: mild gasification, metallurgical coke substitute, mild gasification condensables

INTRODUCTION

Coal is the largest indigenous energy resource in the United States. As consumption of petroleum products and electricity increases in the United States, it becomes increasingly important to develop processes that enable the wider use of coal, including its use as a feedstock for petroleum product substitutes in energy and chemical markets. One such process, called "mild gasification," is under development at the University of North Dakota Energy and Environmental Research Center (EERC) and is similar to the petroleum-refining process in that several coal products are produced that meet the needs of different end users. Thus, within the process economic boundaries, production of a high-value product can be maximized at the expense of a lower value product. The capability to alter product distributions, either by changing feedstocks or processing conditions, permits timely response to the ever-changing market. AMAX Coal Company described the "coal refinery" concept at the Twelfth International Conference on Slurry Technology (1).

In the mild gasification process, for which research is sponsored by the Morgantown Energy Technology Center (METC) of the U.S. Department of Energy (DOE), a rapid devolatilization of coal under mild conditions of temperature and pressure produces three products: a reactive char, a valuable hydrocarbon condensate, and a low-Btu gas. The process under development at EERC would produce activated carbon, metallurgical coke substitutes, diesel fuel additives, and chemical feedstocks.

The objective of the EERC program is to develop a continuous mild gasification process that has the flexibility to enable balancing process economics with the demands of the marketplace. Earlier stages of the program focused on the use of Indiana No. 3 bituminous and Wyodak subbituminous coal in a 1- to 4-lb/hr reactor, to optimize product yields over a variety of reaction conditions. Data generated were used to design and construct a 100-lb/hr mild gasification process development unit (PDU) under Task 4 of the program. This report describes the results of tests performed in the PDU using Wyodak coal.

ECONOMIC CONSIDERATIONS

The economic feasibility of mild gasification is contingent upon obtaining a premium value for the char, probably as a metallurgical coke substitute in the U.S. steel production industry, which is showing signs of economic recovery and is in a position to take advantage of new technology. The value of the condensable hydrocarbon product as a fuel (or fuel additive) is unpredictable and unstable because of dependency on the coal/oil price differential, which was favorable during the oil supply crises in the late 70s and early 80s, but less conducive to coal research during the last eight to ten years.

A new iron-making process developed by Pellet Technology Corporation (PTC) can use mild gasification char in highly reactive iron ore/char pellets that greatly increase throughput in a conventional blast furnace. The pellets can also be used in smaller, more efficient ore reduction equipment such as hot-blast cupolas and direct reduction systems. The competitive char value in the PTC process would be equivalent to that of calcining grade petroleum coke, which is estimated at 30 to 45 dollars per ton, with a market potential of 15 to 20 million tons per year (2).

The best use of the mild gasification condensables may be their conversion to benzene and phenol, which are subject to essentially no market volume limitations and may command prices of \$1.00 and \$2.00 per gallon, respectively (2). The best opportunity for condensables in the transportation fuels' market is as a fuel additive for medium-speed railroad diesel engines. Other possibilities for condensables include their use as feedstocks for production of carbon black (used in rubber goods, pigments, printer's ink, and in the production of carbon electrodes for aluminum ore reduction), creosote, cresylic acid, pitch, and rubber-processing oil, and as a briquetting binder and a coal dust suppressant. The best use of mild gasification process gas (from a 1,000-ton per day facility) will be as on-site plant fuel, with excesses used for cogeneration of electricity. Table 1 shows product specifications for PTC pellets and metallurgical coke and the boiling point fractions obtainable from mild gasification condensables along with their potential uses.

EQUIPMENT DESCRIPTION

The PDU was constructed to provide proof of concept for an integrated mild gasification system operating on specific design coals and to produce char and liquid products for upgrade testing and market evaluation. The system was designed to process 100 lb/hr (dry basis) of feed coal and incorporate capabilities for drying, carbonizing, and calcining caking and noncaking coals in fluid-bed reactors and for separating char, liquid, and gaseous products. The system was designed to enable both integrated operation of the carbonizer and calciner and independent operation of either the carbonizer or calciner. This report deals with tests performed using the carbonizer.

Heat for carbonization is principally supplied by hot flue gas from stoichiometric combustion of natural gas. (In a commercial-scale process, heat would be provided by combustion of process-derived gas and waste coal from a coal-cleaning operation in a fluid-bed combustor.) Provisions for carbonizer steam injection were made to take advantage of the sulfur-removal and condensables quality improvement effects of steam, as seen in previous work (3).

Figure 1 is a diagram of the PDU carbonization area and shows the major components of the system. For operation with Wyoming feed coal, the coal is screened to a size of 1/4 inch by 0. The carbonizer was designed as a spouted bed gasifier, based on favorable results with caking coals in the COALCON and KRW gasifier systems. The operative principle allowing use of caking coal in this design is the dilution of the entering coal by internal recycle of char to the bottom of the tapered bed, where high velocity and low-bed density also reduce agglomeration. Char residence time can be varied by bed height, with the design residence time being 30 minutes. The carbonizer operates at temperatures from 900 to 1500°F (480 to 820°C) with steam partial pressures from 10 to 60% of the total reactor pressure. Feed coal is entrained and fed into the bottom of the reactor using preheated nitrogen (575°F/300°C). Char can be drawn from a variety of locations and injected into a nitrogen-purged tote bin.

The condensables quench and separation system was designed to produce separate tar and oil fractions that meet primary product requirements. In addition, the quench system should provide trouble-free operation without a tendency to plug and, ideally, should produce no wastewater condensables. One objective of this work is to enable recovery from the gas stream of both a tar and an oil product using direct contact tar and oil venturi scrubbers (called the tar scrubber and the sieve tower, respectively) and direct contact water scrubbers. In the venturi scrubbers, the scrubbing liquid is injected into the gas stream above the throat of the venturi.

During operation with Wyoming coal, the tar venturi scrubber was used to remove particulates remaining in the gas stream (that were not removed by the cyclones) and condense boiling point fractions of liquid products ranging in temperature from 350

to 700°F (175 to 380°C). Further cooling occurred in the sieve tower, again using recycled product liquor. This unit operates at an exit temperature just above the dew point of the product gas, approximately 160 to 180°F (70 to 80°C). The product gas then passed through a water scrubber, which cooled the gas stream to 80 to 100°F (27 to 38°C), and a demister to ensure that organic material did not escape and pass through the flare system. (An optional quench system uses two water scrubbers to condense all of the tar, oil, and water from the system before the product gas is flared.)

PRODUCT YIELDS

Table 2 shows product yield and material balance data obtained from Carbonizer Test P010, performed using Wyodak coal. As shown in the table, the char yield was 49 percent of the weight of the moisture- and ash-free (maf) coal fed to the reactor, the condensable yield was 9%, and the gas yield was 42%. The yield calculations involved accounting for the CO₂, N₂, and H₂O contents of the product gas and condensable streams that resulted from the combustion of natural gas to provide system heat.

CHAR ANALYSIS AND METALLURGICAL COKE SUBSTITUTE PRODUCTION

Table 3 shows the results of proximate and ultimate analyses performed on the char products obtained from Test P010. The steel industry has specified that for a coal char product to be suitable for use as a coke substitute, its sulfur and ash contents should be less than 1 and 10 wt%, respectively. Table 3 shows that the Wyodak char meets the sulfur specification and only slightly exceeds the ash limit. Pellet Technology Corporation (PTC) utilized Wyodak char from an EERC test performed under conditions similar to those employed for Test P010 as a metallurgical coke substitute in iron ore-reducing tests. The PTC tests were performed using pellets made from Wyodak char, iron ore, lime, and silica. After pressing, the pellets were dried and hardened. Pellets made with a 10 wt% (of total pellet weight) binder comprised of calcium oxide and silica exhibited satisfactory strength, density, and abrasion resistance.

The results of the ore reduction tests, in which the pellets were subjected to temperatures of 2500 and 2700°F (1370 and 1480°C), showed that iron ore reduction times for char-iron ore pellets could be reduced by as much as 80%, compared to reduction times required for coke-iron ore pellets. The fact that the Wyodak char-iron ore pellets were reduced in about 5 minutes (as opposed to the 25 minutes required for coke-iron ore pellets) is thought to be due to the high reactivity of the Wyodak char.

LIQUIDS ANALYSIS

Simulated Distillation To enable comparison of condensable product streams with petroleum fuels, simulated distillation of each P010 liquid product sample was performed using capillary gas chromatography. The technique works as follows: A condensables sample (liquid or tar) is dissolved in methylene chloride at a concentration of approximately 20 milligrams per milliliter (mg/mL), internal standards are added, and the mixture is injected into a gas chromatograph (GC). The temperature in the GC oven is maintained at 122°F (50°C) for two minutes, after which it is raised to 626°F (330°C) at a rate of 14.4°F (8°C) per minute. The chromatogram obtained is compared with a chromatogram of a carefully prepared mixture of normal alkanes (C7, C8, C9..., C25) obtained under identical chromatographic conditions. Since the boiling point of each alkane is known, the relationship of boiling point to GC retention time can be calculated. Once this relationship is determined, the boiling point of any compound in the sample can be approximated based on a comparison of the unknown compound's GC retention time to the retention times of the alkane standard compounds that "bracket" the unknown compound; i.e., if an unknown compound has a retention time midway between the

retention times of C7 and C8, the compound is assigned a boiling point midway between the boiling points of C7 and C8. After assigning boiling points to all compounds detected in a sample (this operation is computerized because in most samples, about 200 to 400 compounds are detected), a plot is generated of cumulative "area percent" of a sample distilled versus temperature. Area percent refers to how the GC detector quantitates, on a relative basis, each compound in a sample. (In the ASTM D-86 distillation method, the distillate is quantitated on the basis of volume percent distilled.) Comparison of ASTM D-86 and simulated distillation data obtained for Diesel #2 and a sieve tower liquids sample showed that the simulated distillation technique yields boiling-point data that is nearly identical to data yielded by the ASTM method.

Separation of Coal-Derived Material Some of the condensables samples obtained from Test P010 contained not only coal-derived material, but also petroleum products, which were used as start-up fluids in the tar scrubber and sieve tower. Mandan Decant Oil, a heavy fuel oil resid from the Amoco Oil Refinery in Mandan, North Dakota, was circulated through the tar scrubber during reactor heat-up, and Diesel #2 was circulated through the sieve tower. A method is being developed at EERC to determine the amounts of diesel fuel and decant oil in a condensables sample using a computerized chromatogram subtraction technique.

The technique involves determining the contributions of diesel fuel and decant oil to the total chromatogram for a condensables sample. This is done by comparing a condensables sample chromatogram with chromatograms of diesel fuel and decant oil. The diesel fuel chromatogram is multiplied by a factor (between 0 and 1) and the resulting chromatogram is subtracted from the condensables chromatogram. This operation is performed as many times as necessary until a factor is found that yields a "difference chromatogram," with many components having area-percent magnitudes near zero. The factor that yields such a difference chromatogram is then multiplied by 100% to yield the percentage diesel fuel in the condensables sample. The same process is repeated using the original condensables chromatogram and the decant oil chromatogram. Subtracting the factored diesel fuel and decant oil chromatograms from the original condensables chromatogram yields a chromatogram that represents the coal-derived material. A simulated distillation curve can then be constructed from this chromatogram. Figure 2 shows the simulated distillation of coal-derived material (Test P010) from the tar scrubber, sieve tower, and the water scrubber. Based on the chromatogram subtraction technique described above, the tar scrubber condensables were estimated to be 100% coal-derived, the sieve tower condensables 93% coal-derived, and the water scrubber condensables (excluding water) 91% coal-derived. The figure shows that the coal liquids condensed in the sieve tower are lighter than the petroleum liquids, and the coal liquids condensed in the water scrubber are heavier than the petroleum liquids. It must be emphasized that the chromatogram subtraction technique is still under development and more work is needed to ensure its validity.

As-Recovered Condensables Analysis Tables 4 and 5 show results of analyses of the condensables obtained from the test. These tables, along with Table 3, show that the sulfur content of the char products is roughly equal to that of the feed coal, and that the sulfur contents of the tar scrubber and sieve tower liquids were significantly higher than that of the feed coal. The reason for the high-sulfur concentrations of these liquids is that they contain not only coal-derived condensables, but also the decant oil and/or diesel fuel start-up fluids. As shown in Table 5, the sulfur content of the decant oil is about 1.9%. On the basis of the sulfur contents of the tar scrubber and sieve tower liquids, it can be inferred that these liquids, with the possible exception of TS-3 (the latest tar scrubber sample obtained), contain some petroleum products.

Proximate analysis was performed on the tar scrubber samples since these samples likely contained significant amounts of coal fines that were not removed by the cyclones. Figure 3 compares the fixed carbon and ash contents of the tar

scrubber liquids with the ash content of tetrahydrofuran (THF) insolubles from the tar scrubber liquids. The linear increases in the THF-insoluble and ash contents indicate that the THF-insolubles are coal fines and not polymerized tar compounds. This buildup of coal fines occurred because insufficient amounts of coal liquids were being condensed into the tar scrubber recycle cooling fluid to fill the unit to the level at which recycle coolant is pumped out of the system.

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TABLE 1
CHAR PRODUCT SPECIFICATIONS AND CONDENSABLES USES

	PTC Process ^a	Formcoke
% Volatile Content	12	3-6
% Ash	10	10
% Sulfur	<1	<1
<u>Condensable Boiling Point Fractions</u>		
ibp - 330°F	Gasoline Octane Enhancer, Benzene	
330° - 430°F	Cresylic Acids, Phenols	
430° - 700°F	Diesel Fuel Blends	
700° - 1020°F	Briquetting Binders, Anode Carbon	

^a Pellet Technology Corp. Process

TABLE 2
CARBONIZER MATERIAL BALANCE & YIELD SHEET

	1	2	3	4	5	6
	KG In	KG CH ₄ Comb. Prod.	KG Out	Yields	N Yields	Vol. %
MAF (Coal/Char)	509		506	99	49	
H ₂ O in (Coal/Char)	181		4	-35	-35	
H ₂ O in (Steam/Cond.)	0		317	62	49	
H ₂ O in Gas		165	100	-13	-13	
H ₂ O Total					0	
Ash	35		67	6	0	
Cond. Total			63	12	9	
ibp-165			0	0	0	
165-220			9	2	1	
220-375			28	5	4	
375-550			28	5	5	
550-1000			-2	0	0	
BP>1000			0	0	0	
Char Fines			0	0	0	
Residue			0	0	0	
Gas Total	2,698	2,533	2,846	62	42	
H ₂			9	2	2	4.6
CO ₂		202	546	67	64	12.5
C ₂ H ₆			3	1	1	0.1
H ₂ S			1	0	0	0.0
C ₂ H ₄			4	1	1	0.2
C ₂ H ₂			5	1	1	0.2
O ₂	529	-294	0	-46	-46	0.0
N ₂	2,096		2,201	21	5	78.9
CH ₄	74	-74	30	6	6	1.9
CO	0		47	9	9	1.7
Btu/scf						45.2
KJ/L						1.7
scf/100 lb						6,974.0
SL/100 Kg						370,548.8
Total	3,424	3,424	3,903	194	100	
Mat. Balance			114.0			

Run No.	P010	1	Mass into the system
Feed Coal	Wyodak	2	Mass change due to the combustion of natural gas
Temperature	1100°F	3	Mass out of the system
Pressure	14.7 psia	4	Yields based on MAF coal feed
Res. Time	0.50hrs	5	Normalized yields based on 100% material closure
		6	Product gas composition out of condensation train
Fluidization Gas:	Natural Gas with 80% Excess air, 6% Steam, 78% N ₂ , 7% CO ₂ , 0% CO, 0% H ₂ , 9% O ₂ , 100 Total		
% loss to gas	22.00		% loss to char off-take leg 61.00
% loss to tank 504	17.00		% loss to primary/secondary cyclone 0.00

TABLE 3
ANALYSIS OF PO10 WYODAK COAL CHAR

	Feed Coal 1/4 x 0	Product Char 1	Product Char 2	Primary Cyclone Char
Proximate Analysis (wt%)				
Moisture	25.0	0.3	0.8	3.7
Volatiles	33.8	18.5	17.6	18.5
Fixed Carbon	36.3	69.5	69.9	66.8
Ash	4.8	11.7	11.7	11.0
Ultimate Analysis (wt%)				
Hydrogen	6.2	2.6	2.3	2.7
Carbon	51.0	78.6	78.3	76.1
Nitrogen	0.7	1.3	1.3	1.3
Sulfur, mf ¹	0.4	0.7	0.5	0.5
Oxygen	36.8	5.2	5.9	8.4
Ash	4.8	11.7	11.7	11.0
Heating Value (Btu/lb)	9,065	12,582	12,355	12,134

¹ Moisture-free basis.

TABLE 4
ANALYSIS OF PO10 TAR SCRUBBER LIQUIDS¹

Proximate Analysis (%)	IS1 ²	IS2	IS3
Moisture	0.6	0.1	0.4
Volatiles	79.0	74.0	62.9
Fixed Carbon	17.9	22.8	31.8
Ash	2.5	3.2	4.9
Sulfur (wt%)	1.5	1.4	1.3
THF-insolubles (wt%)	17.1	18.6	29.6
Melting Point (°C)	53.0	65.0	85.0

¹ The tar scrubber "liquids" were solid at room temperature.

² Tar scrubber samples 1-3 were collected at 8-hour intervals during the test.

TABLE 5
ANALYSIS OF P010 SIEVE TOWER AND WATER SCRUBBER LIQUIDS

	<u>ST1</u>	<u>ST2</u>	<u>ST3</u>	<u>Diesel #2</u>	<u>Decant Oil</u>
Sulfur, wt%	1.2	1.2	0.9	0.0	1.9
		<u>WS1</u> <u>Organic</u> ²	<u>WS2</u> <u>Organic</u>		<u>WS3</u> <u>Organic</u>
Water Content, wt% ³		22.3	13.9		0.2
		<u>WS1</u> Aqueous	<u>WS2</u> Aqueous		<u>WS3</u> Aqueous
Phenolics, mg/L ⁴					
Phenol		4,800	4,300		2,500
Cresols		3,100	2,130		1,300
C2-Phenols		500	340		220
Total Phenols		8,400	6,770		4,020
TOC ⁵ , mg/L		6,800	6,300		5,170

¹ Sieve tower samples 1-3 were obtained at 8-hour intervals from bottom tray of sieve tower.

² Water scrubber samples 1-3 were obtained at 8-hour intervals. Each sample contained an organic and an aqueous phase. The organic phase comprised 14, 14, and 18 wt% of the WS1, WS2, and WS3 samples, respectively.

³ Values determined using Karl Fisher analysis.

⁴ Values estimated using gas chromatography/flame ionization detection.

⁵ Total organic carbon.

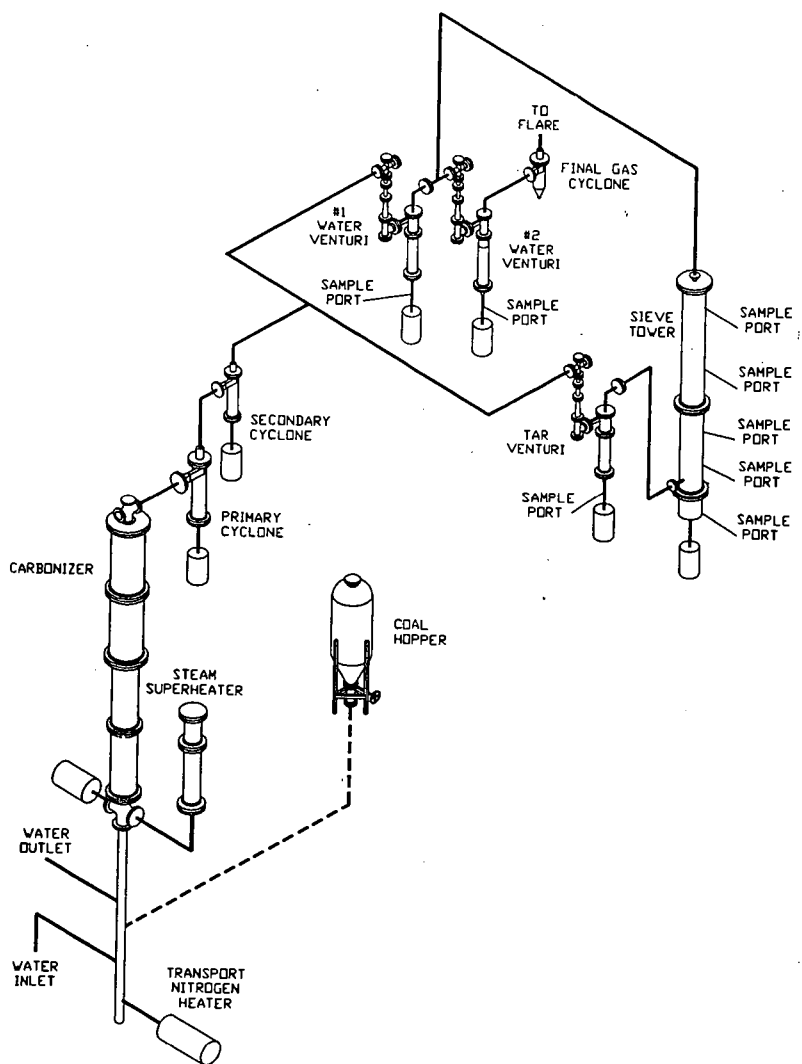


Figure 1. Diagram of the PDU carbonization area.

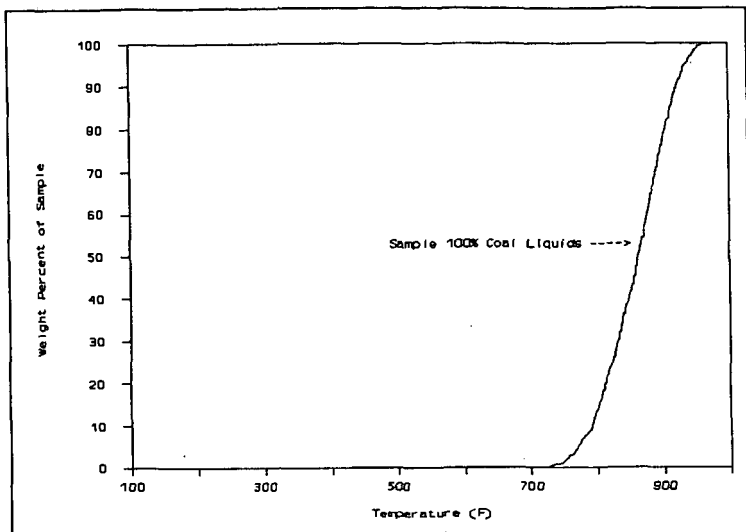


Figure 2a. Simulated distillation of coal liquids condensed in tar scrubber.

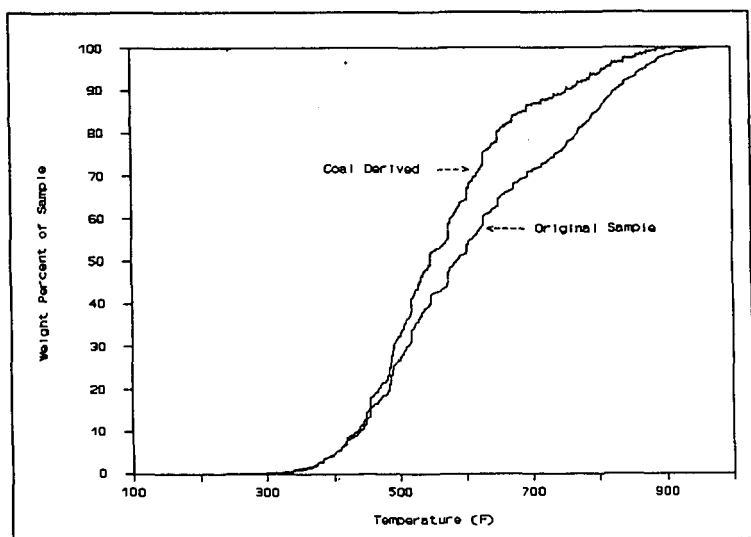


Figure 2b. Simulated distillation of coal liquids condensed in sieve tower.

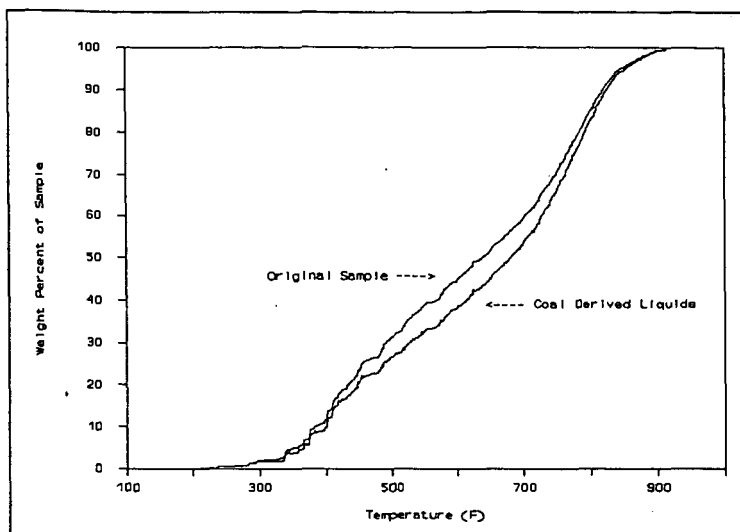


Figure 2c. Simulated distillation of coal liquids condensed in water scrubber.

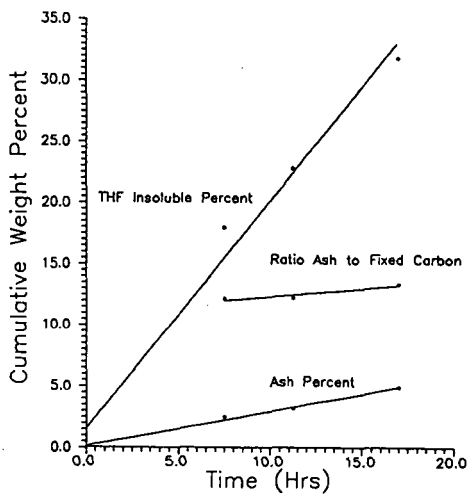


Figure 3. Weight percent of coal fines in tar scrubber liquids.